Internal Report

Assessment of High-Rate Sedimentation Processes: Microcarrier Weighted Coagulation Jar Tests

by

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Disclaimer

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It has been subjected to the Agency’s technical peer review. Currently, the microcarrier weighted coagulation jar test procedure is being further evaluated. It does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Also, the mention of trade names or commercial products does not imply endorsement by the United States government.

Abstract

Past studies have identified that a significant amount of wet weather flow pollutants is associated with colloidal and larger particulate solids. These particles can play an important role in water treatment and pollutant transport due to their large specific surface area and high energies that facilitate the sorption of significant quantities of substances. Since the colloidal particles adsorb heavy metal and organic ions and water borne microorganisms, removal of these particles is of paramount importance in the water treatment process. In this process, colloidal particles, coagulated with microcarriers (MC), can be removed by a high-rate sedimentation process. The MC plays a crucial role in enhancing settling properties, and in particular, the removal of colloidal particles and associated contaminants.

A detailed testing procedure and a method of experimental analysis using a modified jar test for the MC process have been developed. A series of MC weighted jar tests were undertaken on parking lot storm runoff, synthetic samples, and combined sewer overflow mixed with a MC, coagulant (electrolyte) and coagulant aid (polyelectrolyte). Two particle analyzers with a range of 0.002 to 5 micrometers (μm) and 0.1 to 2,000 μm, respectively, were used to determine the full range of particle size distribution. Different materials were used as the MC in this study. The operational parameters being evaluated include coagulant dosage, coagulant aid type and dosage, mixing- and flocculation-induced hydraulic shear or velocity gradients and duration, and characteristics of the MC. The pH, turbidity, particle size distribution, total solids, total volatile solids, suspended solids, and zeta potential were determined. The experimental results reveal that the MC weighted coagulation dramatically reduced coagulation (< 3min.) and settling time (< 8 min) producing high settling velocity flocs and high quality supernatant (turbidity from > 80 to < 2 NTU).

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Chapter 1
Introduction

1.1 Background

Urban wet-weather flow (WWF), which includes sanitary sewer overflow (SSO), combined sewer overflow (CSO), and stormwater discharge (SWD), contains significant quantities of toxic substances. WWF related toxic pollutants are major contributors to the degradation of receiving waters. Urban WWF contains a greater variety of toxic pollutants than sanitary wastewater. Pollutants carried off urban catchments by drainage systems during wet weather originate from many sources, e.g., commercial, industrial, and residential parking areas; roadways; automobile-service stations; sewer infiltration from leaking underground storage tanks; accidents and spills; park and residential lawns; construction sites; and active and inactive industrial sites. Past studies indicate that SSO, CSO, and urban SWD contain significant quantities of toxic substances; a number of the hazardous-waste priority pollutants have been identified. Without consideration of urban and industrial stormwater-runoff toxic-substance control, the various hazardous-substances-cleanup programs will not be effective in controlling total area wide emissions of these substances.

Toxic-organic chemicals (e.g., benzene, polynuclear aromatic hydrocarbons [PAH], polychlorinated biphenyls [PCB], etc.) and heavy metals (arsenic [As], cadmium [Cd], chromium [Cr], copper [Cu], lead [Pb], mercury [Hg], and zinc [Zn]) in storm-induced discharges contribute to receiving-water degradation (Pitt, et al., 1995). The US Geological Survey reported that urban storm runoff collected from residential, commercial, and industrial areas around Phoenix, AZ was found to be toxic to fathead minnows and water fleas (Lopes and Fossum, 1995). Industrial and commercial parking lots, material storage areas, and vehicular service stations are the most significant contributors of such pollutants to WWF as reported by Pitt, *et al*.(1995).

Sansalone *et al*. (1995) observed that lead, predominantly associated with the particle fraction, was more mobile than copper for highway runoff. Water quality in a creek below a highway construction site indicated that the sediment concentrations of total hydrocarbons, aromatic hydrocarbons, and heavy metals and water concentrations of heavy metals and selected anions increased downstream of roadway runoff (Maltby *et al*. 1995). Hydrocarbon contamination of sediments was positively correlated with potential contaminant loading functions (that is, length of road drained/stream size). Boudries, *et al.* (1996) and Estèbe, *et al*. (1996) reported that heavy metals and aliphatic and aromatic hydrocarbons bound to particles in the River Seine sediments near Paris are due to urban WWF discharges. Such toxic

substances in sediments create a long-term impact on ecological systems.

Most of the solids finer than 50 micrometers(μm)are the principal vector of pollution in urban stormwater (Chebbo *et al., 1990*). Table 1-1 that summarizes results from urban storm runoff characterizations by Ellis and Revitt (1982) and Vignoles and Herremans (1995) indicates the majority of heavy metals are associated with particles less than 10 μm which are well into the colloidal range. Thus, in order to effectively control toxic heavy metals in urban stormwater, treatment processes that are capable to remove fine particles (<10 μm)and to be able to handle unsteady-nonuniform stormwater flow must be used. However, very few of the commonly applied physical-chemical processes are cable to remove such fine particles effectively.

Table 1-1. Metal Distribution Versus Particle Size

Suspended solids Size (micrometers)	Metal Distribution (%)							
	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
> 100	18	9	5	7	8	8	4	5
10 -- 100	36	31	24	30	21	29	23	35
< 10	46	60	71	63	71	63	73	60

One approach of removing small particles in urban WWF is to apply coagulant to promote colloid sorption during floc formation prior to sedimentation than followed by filtration. These processes achieve better solids removal than the plain sedimentation (retention tank); but unsteady stormwater flow can detrimentally affect the process efficiency. In recent years, micro-sand has been used as weighted microcarrier (MC) in ballast-coagulation of colloidal particles accelerating settling velocity. This is a new high-rate physical-chemical clarification process. It was originally designed for drinking water treatment and recently being tested for treating wastewater and WWF. This process consists of the addition of a coagulant in the influent pipe, MC and coagulant aid (i.e., flocculant, polymer, polyelectrolyte) in a mixing chamber, and than followed by maturation (flocculation) and sedimentation tanks. The initiation of the reaction of coagulation-flocculation processes is improved by the presence of the MC and polymer, which increases the bonding of the floc to

the MC, resulting in higher settling velocities. The Microsep® (U.S. Filter Corporation) and the Actiflo® (Omnium de Traitement et de Valorisation [OTV]) are two commercially available systems that use recycled MC (e.g., microsand), while DensaDeg® (Infilco Degremont, Inc.) recycles its sludge. Recently, these processes are being evaluated at an increasing number of pilot units for treating CSO.

1.2 Purpose of Study

In view of the difference between MC and conventional coagulation-flocculation processes, the existing bench-scale testing procedures or standard Jar Test may not be adequate. Thus, there is a need for developing a new set of bench-scale testing procedures. The main purpose of this study is to develop and evaluate new MC bench-scale (Jar Test) procedures for engineers or plant operators to screen and select the effective combination of type-dosage of coagulant, MC, and coagulant aid for removing WWF colloidal particles. Determination of the particle size distribution and zeta-potential of colloids enable a better selection of coagulation-flocculation agents for the MC weighted coagulation process. Results of the experimental study herein may offer useful information to provide a framework for further evaluation on MC weighted coagulation for subsequent researchers.

Objectives

The objectives of this investigation are to:

- Evaluate the applicability of conventional jar test procedure to the MC weighted coagulation, and if needed, modify the jar test procedure for screening MCs, coagulants, and coagulant aids;
- Test the effects of different types and dosages of coagulant and coagulant aid in conjunction with MC for selection of the most effective combination;
- Investigate the effect of MC on particle size distributions and zeta potential of colloids in urban WWF by using the modified jar test procedure.

Presented below is a brief review related to the phenomenon of coagulation.

1.3 Colloids Coagulation Analysis

Colloid coagulation is a complex process which depends on a number of factors such as colloid type, particle concentration, pH, coagulant concentration, particle size distribution, surface area, surface charge, interfacial reactions and collisions between suspended particles (Gregory, 1993). Mathematically, the

coagulation process is known to be a binary process that has been modeled as a second-order rate process (for example, O'Melia, 1993): $dn/dt = kn^2$, where n is the concentration of particles in suspension at time t, and k is a second order rate constant. From a mechanistic point of view, coagulation depends on two distinct influences: (a) particles must move in such a way that collision occurs; and (b) interaction between colliding particles must be such that permanent contacts can be formed. These two factors are related to the rate constant mathematically as $k = \alpha\beta$, where α is a dimensionless sticking coefficient associated with the colloidal stability while β is a mass transport coefficient depending on the transport mechanics and their particle interactions. Various approaches have been proposed for determining these coefficients. In general, β is evaluated from a micro-hydrodynamics standpoint and α is determined indirectly from experimental results. It should be pointed out that although micro-mechanisms of colloidal particle coagulation have been studied extensively for chemical and biological applications, interest in water and wastewater treatment applications only began in the late 1960's. In any case, the interest in environmental studies was provided by the advances in environmental engineering, especially in the theory of interparticle forces, coupled with the development of new experimental techniques.

Mass Transport Coefficient (β)

Suspended particle collisions occur in water due to velocity variations caused by three different processes, namely, Brownian diffusion, fluid shear, and differential settling. Generally, particles less than 0.1 micrometer in diameter may be dominated by Brownian diffusion while particles larger than about 5 micrometers may be transported by settling. Particles in the range of 0.1 to 5 micrometers are too large for Brownian diffusion and too small for settling.

By assuming that all particles move in straight lines until contacts occur between them, a rectilinear model was established by Smoluchowski. The expressions of β for each of the three different transport mechanisms have been determined analytically (e.g., Clark, 1996). This model is considered to be the most fundamental approach in colloidal coagulation analysis. However, the rectilinear model neglects the hydrodynamic influence and the short-range interactions between approaching particles. Moreover, as aggregates grow in size, transport mechanisms change, aggregate morphology is altered, and breaking up by hydrodynamic forces can occur. Recently, questions were raised with regard to the validity of the rectilinear modeling approach. Han and Lawler (1991) modified this model using a curvilinear track for particle motions by adding hydrodynamic considerations.

However, interparticle reactions have not been included in the analysis.

Colloidal Stability (α)

Given the possible collisions between particles, stable particles have to be transformed into unstable ones in order to complete the coagulation process. Experiments to determine the colloidal stability in aquatic systems are scarce. Theories about the origins of colloidal stability in aquatic systems are few and qualitative and none has been tested experimentally. The present status is described well by Professor O'Melia: "Theories of colloidal stability are helpful in understanding why particles are stable and in identifying important chemical properties of solutions and solids that affect stability, but they are not able to provide accurate quantitative predictions of coagulation rates when chemical repulsive interactions produce low attachment probabilities (low alphas)." (O'Melia, 1993).

Particle Interactions

The earliest and still the only quantitative analysis of colloid stability is the DLVO theory, developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). Essentially, they combine the Van Der Waals attraction (caused by dipole moments in the constituent molecules of two approaching colloidal particles) and the electrical double layer repulsion to give the total energy of interaction between particles as a function of the separation distance. All other types of interactions are ignored. In addition, the theory is dependent on factors such as colloid type, particle concentration, pH and coagulant concentration.

Analytical formulation of the double layer was developed independently by Gouy and Chapman who derived the fundamental equation relating electrical potential to charge in the diffuse layer (Russel, et al, 1989). The potential at the plane of shear within the double layer is known as the Zeta potential. It depends on the thickness of the double layer and its value determines the extent of the electrostatic forces of repulsion between charged particles. The seta potential is a useful and important tool in providing information on the optimum coagulant dosage for the microcarrier process.

Fractal Approach

The problem of characterizing particle size becomes somewhat complicated for natural particles and their random aggregates. Fractal theory has been explored to study this process (e.g., Lin, et al., 1989; Meakin, 1988). Since random aggregates contain greater surface area than any equivalent sphere or other

shape, the aggregate is more of a 'tenuous' surface (two-dimensional) rather than a three-dimensional object. For a large number of aggregates, if the mass is plotted against aggregate size on a log-log scale, the plot may be linear with a non-integer slope. The relationship between aggregate mass *(M)* and size *(L)* can be expressed as $M = L^d$, where the 'slope' *(d)* of the line is called the fractal dimension. For a regular two or three-dimensional object, the slope is either two or three, respectively. The lower the fractal dimension, the more open the aggregate structure. As the coagulation of solid particle proceeds, fluid is incorporated into pores in the aggregates that are formed. Aggregate density decreases and total aggregate volume increases as the process continues. The result is that the target cross sections or collision diameters of the aggregates increase thereby increasing the rates of interparticle contact brought about by Brownian diffusion, fluid shear and differential sedimentation. Observations of natural and technological systems indicate that the aggregates in these systems are fractals and have fractal dimensions less than three.

Relevant Aspects

In the past, considerable attention has been given to describing airborne-particle capture in flow past simple collector geometries, especially cylinders (Pruppacher and Klett, 1978; Wen, 1996). There are similarities between the capture of gas-borne particles and liquid-borne particles based on computed forces from fluid mechanics theory. However, important dissimilarities exist for kinds and magnitudes of other forces not based upon the field of fluid mechanics such as electrostatic force. Other factors such as different molecular mean free paths for gases and liquids also play an important role in the coagulation process.

1.4 Organization of Report

This report consists of six chapters and two appendixes with associated references. First, Chapter 1 presents a background review on the MC process followed by statement of the primary objectives of the study and a brief review of colloid coagulation phenomena of colloids related to water treatment. Chapter 2 describes the major apparatus, instruments and testing procedures used in this study. The experimental program is presented in Chapter 3, which includes sample preparation and three stages of experimental design, namely, prescreening, screening, and confirmative tests. Chapters 4 and 5 present experimental results for surface runoff and CSO jar-tests, respectively. Summary and recommendations are discussed in Chapter 6. Appendix A presents a quality assurance statement. Appendix B describes the zeta potential measurement procedures recommended by the manufacturer. In addition, experimental results are presented in Appendix C.

Chapter 2

Experimental Instruments and Testing Procedures

2.1 Test Apparatus and Instruments

The descriptions for the major test apparatus and analytical instruments used for the investigation, including the measured parameters, range, model number, and manufacturer, are listed in Table 2-1 and briefly described as follows:

- Particle size analyzer I, designated as PSA-I, is a large scale particle size analyzer with a measurement range from 0.1 to 2000 μm. Figure 2-1 is a photograph of the PSA-I instrument.
- Particle size analyzer II, designated as PSA-II, is a small scale particle size analyzer with a measurement range from 0.002 to 5 μm. PSA-II is equipped with disposable sample cells that eliminates the cross sample residue influence. Figure 2-2 is a photograph of PSA-II instrument.
- Zeta potential meter. The zeta potential meter and PSA-II are integrated in one unit. The measurement range of the zeta potential meter is from 0.1 to 200 mV with the particle size range from 0.002 to 30 μm. The resolution is sample dependent and in the range of 0.1% to 5%.
- Jar test apparatus: A Phipps and Bird (Model PB-700™ as shown in Figures 2-3 and 2-4) was used. Dimensions of each jar are 11.5 X 11.5 X 21 cm depth which is capable for testing a volume of 2,000 ml water sample. Each jar is equipted with a flat stirring paddle (7.6 X 2.5 cm or 19.3 cm^2). For MC jar test, the area of the paddle was increased to 38.7 cm^2 for MC jar test in order to generate more rigorous turbulence for keeping micro-sand in suspension.
- Turbidity meter.
- pH meter.
- Balance.

Table 2-1. Specifications of Major Instruments

Apparatus/ Instrument	Measurement Parameter	Measurement Range	Model No.	Manufacturer
PSA-I	Particle size	0.1—2000 μm	Master-Sizer X	Malvern Instruments Inc. Southborough, MA
PSA-II	Particle size	0.002—5 μm	90 Plus combined with ZetaPlus	Brookhaven Instruments Corporation Holtsville, NY
Zeta potential meter	Zeta potential	0.1—200 mV		
pH meter	pH	1—14		
TOC Analyzer	TOC	4—10000 ppb	700 TOC	O.I. Analytical College Station, TX
Stirrer	Jar Test	0—300 rpm	PB-700™ Jar tester	Phipps & Bird Richmond, VA
Turbidity meter	Turbidity	0—1000 NTU	DRT-15CE	HF Scientific Inc. Fort Myers FL
Balance	Weight	0—210 grams	XS-210	Denver Instrument Co. Arvada, CO

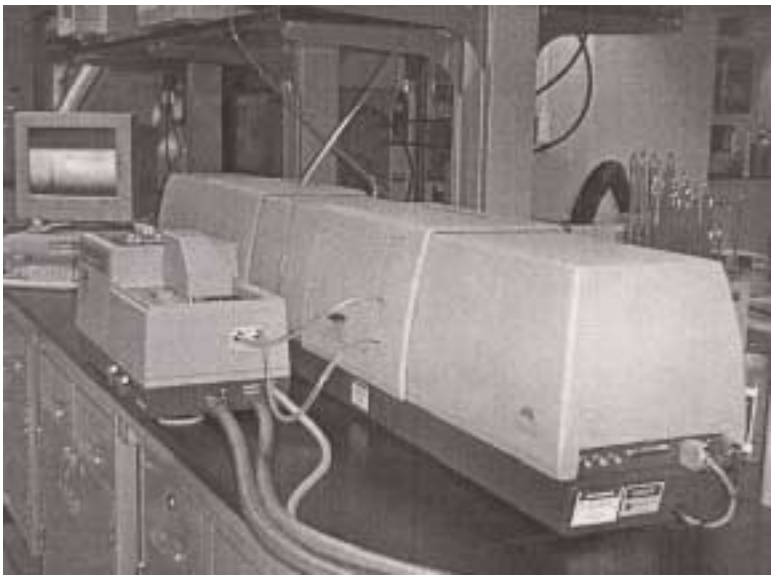

Figure 2-1. Particle size analyzer

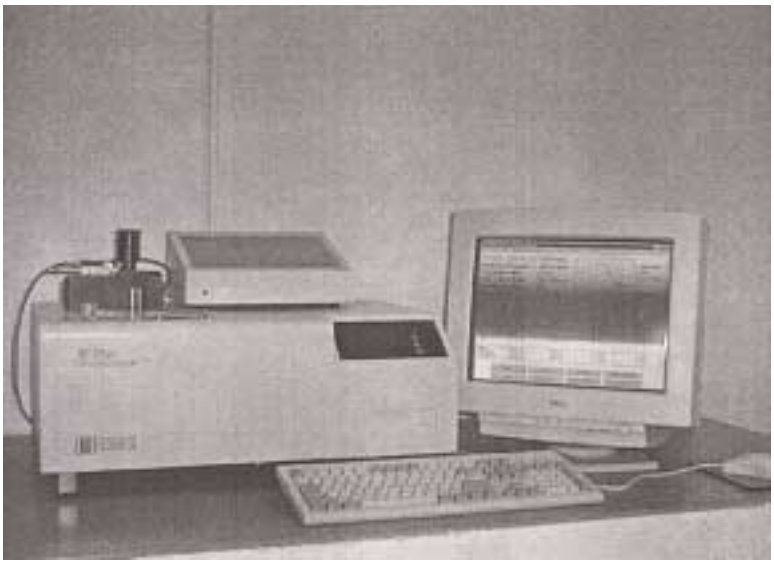

Figure 2-2. Particle size analyzer II with zeta potential meter

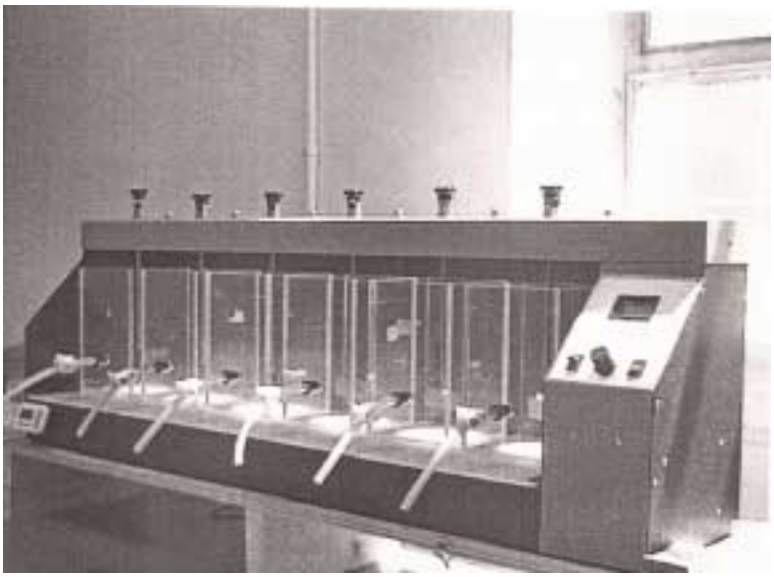

Figure 2-3. Six stirrer jar apparatus

2.2 Testing Procedures

With the exception of zeta potential measurement, all parameter measurement procedures were based on USEPA procedures or Standard Methods. The measurement procedures are summarized in Table 2-2.

Table 2-2. Parameter Measurement Procedures

Parameter	Sample Type	Method No.	Method Title	Reference
Particle Size	Stormwater Microcarrier	2560	Particle count and size distribution	Standard Methods[1]
Zeta Potential	Stormwater	Appendix B	Zeta potential measurement	Manufacturer
MC Weighted Jar Test	Stormwater Microcarrier	I-1	Coagulation and flocculation	AEEP[2] (modified)
pH	Stormwater	150.1	pH (electrometric)	EPA[3]
Volatile Solids	Stormwater	160.4	Residue, Volatile	EPA[3]
Turbidity	Stormwater	180.1	Turbidity (Nephelometric)	EPA[3]
Suspended Solids	Stormwater	160.2	Residue, Non-filterable	EPA[3]
Total Solids	Stormwater	160.3	Residue, Total	EPA[3]

[1]Standard Methods, 18th edition supplement (1995). [2]Environmental Engineering Unit Operations and Unit Processes Laboratory Manual, Association of Environmental Engineering Professors (1971). [3]Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (1983).

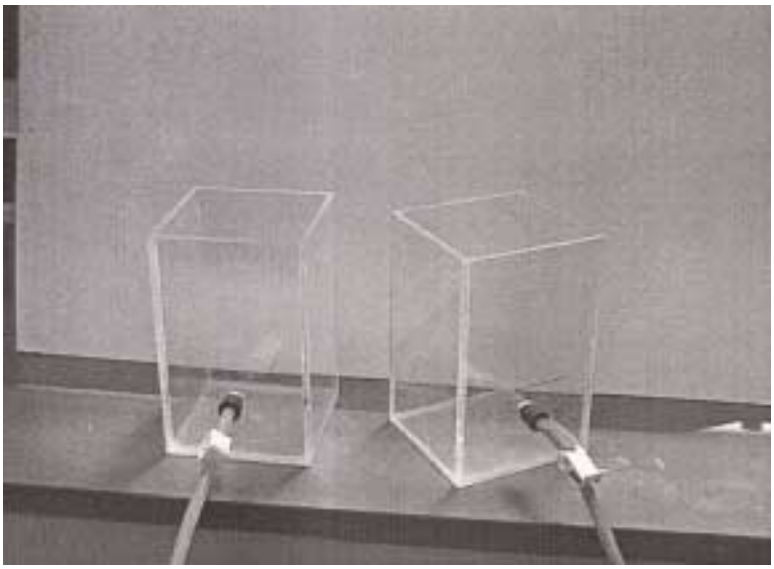

Figure 2-4. Square jars

MC Weighted Jar Test

The jar test has been used as a method for evaluation of the effectiveness of coagulants and coagulant aids for removal of solids in water treatment for many decades. Detailed jar test procedure can be found in numerous publications (Cohen, 1957; Black et al., 1957, 1969; Camp, 1968; AEEP, 1971; ASTM, 1996). However, the MC weighted jar test is a new application due to the different physical characteristics of the mixture.

In the MC weighted jar tests, water samples of equal volume (1,000 ml) were poured into a series of six 2-litter square beakers on a multiple stirring machine equipped with a variable speed drive. After precalculated dosages of the microcarrier, coagulant, and coagulant aid (i.e., flocculant, polymer, or polyelectrolyte) had been added to the beakers, the contents were rapidly stirred to simulate flash mixing and then reducing stirred to simulate flocculation. After a given period of time, the stirring was stopped and the floc formed was allowed to settle.

During the process, illumination aids were used in watching floc formation; however, heating effects from the light were avoided. The controlling parameters are enumerated as follows:

1. The volume of the sample.
2. The size and shape of the container.
3. Peripheral speed and time of rapid mixing.
4. Peripheral speed and time of slow mixing.
5. Type and dosage of microcarrier, coagulant and coagulant aid (i.e., flocculent, polymer, or polyelectrolyte).

The principal procedures include the following steps:

1. Collect storm surface runoff sample, prepare synthetic sample (see Section 3.1), or CSO sample. Measure the sample for pH value and turbidity reading.
2. Pour 1,000 ml of the water sample into each two-liter jar on the jar-test apparatus and check stirrer operation. A light table facilitates viewing of the contents of the beakers.
3. Add controlled amounts of MC, coagulant, and flocculant dosage to the designated jars.
4. Flash mixing for 20——60 seconds at 100——200 rpm.
5. Slow mixing for 10——120 seconds at 30——60 rpm. Record the elapsed time before a visible floc is formed. If large flocs are formed, it may be desirable to reduce the paddle speed. Record the appearance of the floc formed.
6. After flocculation, remove the paddles and settle for 2——30 minutes.

7. Collect the supernatant from the sampling port on each jar and measure the turbidity; the settled solids should not be disturbed during sampling. Select and recored the dosage of coagulant and flocculant based on the supernatant clarity and settleability of floc.

Particle Size Determination

Principle

Both particle size analyzers (PSA-I and PSA-II) used in this study are based on light-scattering techniques using a Helium-Neon laser as the light source. However, the signal collection and conversion for the two instruments are different.

In the PSA-I system, the direct path of the light beam through the flow cell is scattered by a particle as it flows through the measurement zone with the fluid (see Figure 2-5). Scattered light over a fixed range of angles is collected by a photo-voltaic cell. Based on the principles of Fraunhofer diffraction, particle size can be determined from the angle (θ) and intensity (I) of scattering as follows:

$$I \propto \frac{\alpha^2 J_1^2(\alpha \sin\theta)}{\sin^2\theta} \quad ; \quad \alpha = \frac{2\pi a}{\lambda}$$

where a is the particle radius; J_1 is the first order Bessel function; and λ is the wavelength. For multi-particles, the resulting responses from all particles are collected and mathematically deconvoluted to generate the size distribution.

In the PSA-II system, the scattered light is collected at a 90 degree angle to the light source (see Figure 2-6). The photon correlation spectroscopy of quasi-elastically scattered light technique, based on correlating the fluctuations about the average scattered light intensity, is the measurement mechanism. The total measurement time is divided into small intervals called delay times. These intervals are selected to be small compared

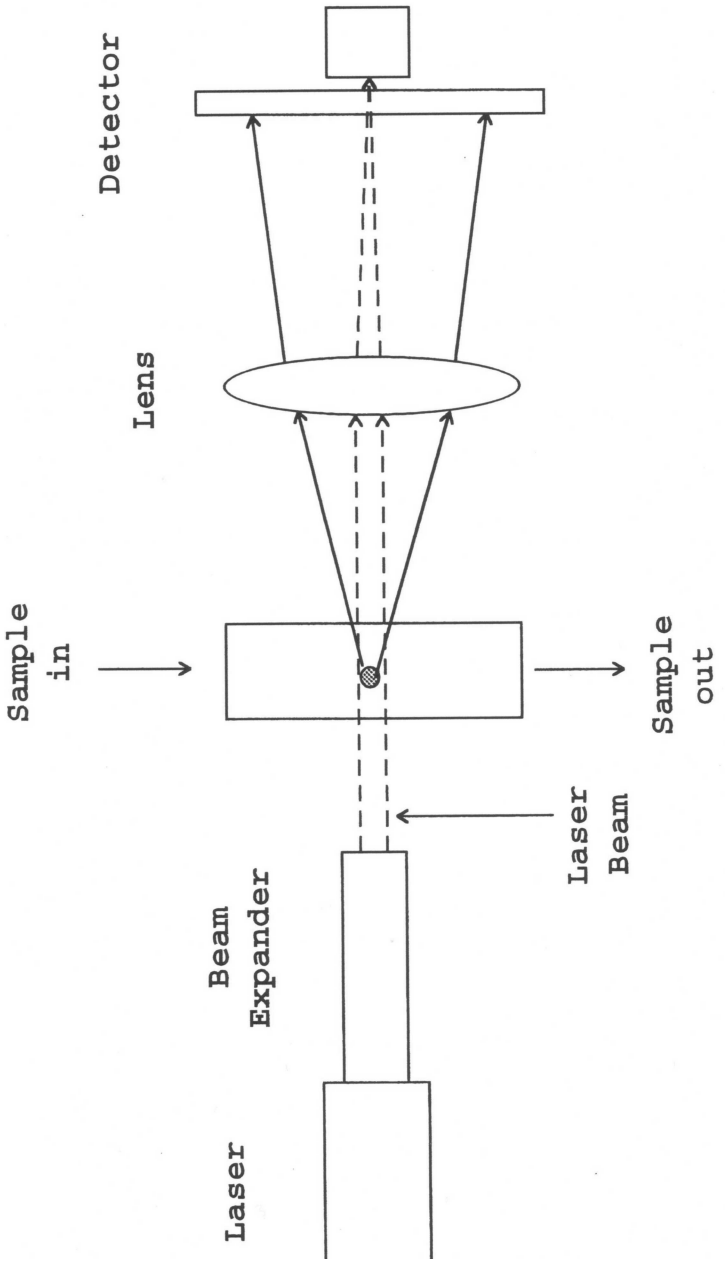

Figure 2.5 Principles of Particle Size Analyzer I

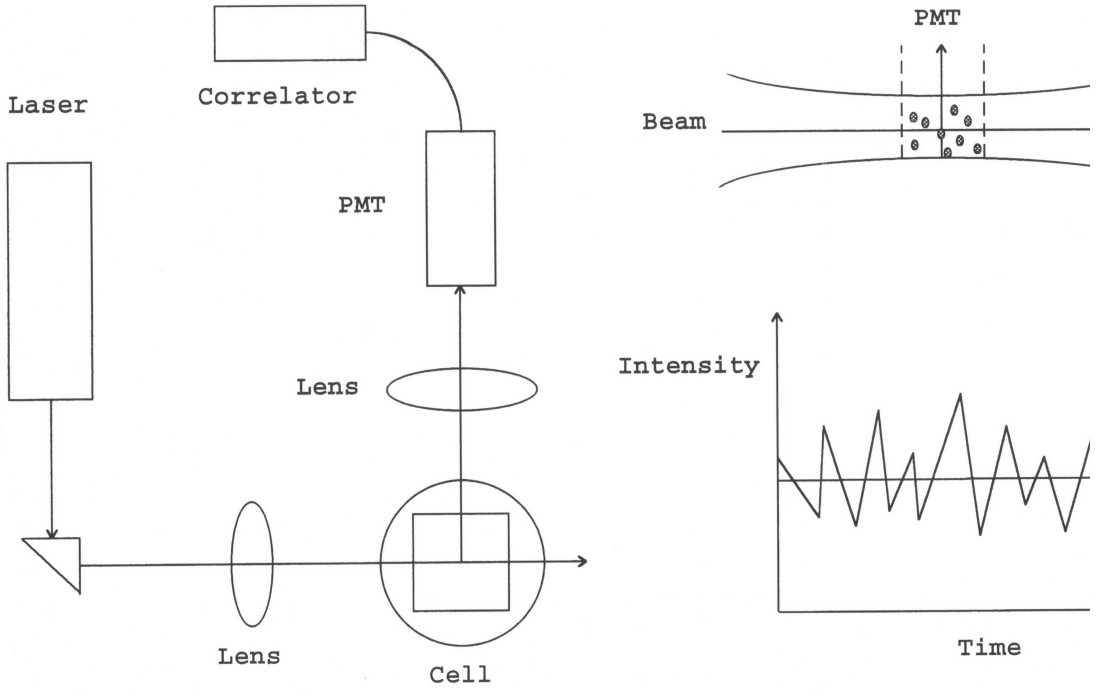

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Figure 2.6 Principles of Particle Size Analyzer II

with the time it takes for a typical fluctuation to relax back to the average. The scattered light intensity in each of these intervals, as represented by the number of electrical pulses registered during each delay time, fluctuates about a mean value. The intensity auto-correlation function is formed by averaging the products of the intensities in these small time intervals as a function of the time between the intervals (delay times). As the delay time increases (t), the correlation (c) decreases and the function approaches the constant background term B. In between these two limits the function decays exponentially for a monodisperse suspension of rigid, globular particles and is given by

$$c(t) = Ae^{-2\Gamma t} + B$$

where A is an optical constant determined by the instrument design, and Γ is related to the relaxation of the fluctuations by

$$\Gamma = D\,q^2$$

where D is the transitional diffusion coefficient. The value of q is calculated from the scattering angle (θ = 90 degrees), the wavelength of the laser light ($\lambda = 0.635$ μm), and the index of refraction (n) of the suspending liquid. The equation relating these parameters can be expressed as

$$q = \frac{2\pi n}{\lambda} 2\sin\left(\frac{\theta}{2}\right)$$

For a sphere, there is

$$d = \frac{kT}{3\pi\eta D}$$

where d is the particle diameter; k is Boltzmann's constant; T is the temperature; and η is the viscosity of the liquid in which the particle is moving. The above equation is based on the assumption that the particles are moving independently of one another. In case a particle is not spherical, the d calculated from the above equation is considered as a particle size indicator.

Measurement Procedure

The principal steps for particle size distribution measurement, in accordance with the Standard Methods For Examination of Water and Wastewater (Standard Methods, 1995), are enumerated as follows:

1. Preparation. The instrument and any sample handling unit should be switched on and any connections between the optical unit, sample handling unit and computer should be in place. The correct range lens should be fitted to the

instrument and the lens caps removed. Any sample cell should be correctly fitted and the windows should be clean. In particular, the correct instrument range should be selected.

2. Background measurement. A background measurement is necessary before any sample measurement.
3. Blank sample measurement. Measure at least one blank sample of particle-free water.
4. Calibration. Calibrate by determining the channel number into which particles of known size are sorted by the instrument. Use spherical particles manufactured for this purpose. Use three sizes of calibration particles in similar concentrations to calibrate a sensor. Calibrate under conditions identical with those of the sample measurement, e.g., settings on the instrument, flow rate, and type of sample cell.
5. Measurement of samples. The light scattered by the particles must be measured for a suitable period to ensure that all particles are represented in the measurement and to average out fluctuations caused by the dispersing medium. A suitable measurement period is 10 to 30 seconds depending on the size range of the distribution.
6. Data reporting. Particle concentrations should be shown in both tabular and graphical formats.

In the course of experiments, it was found that the large particles (> 5 μm) produced interferences during the measurement of small particles (< 5 μm). Furthermore, the measurement of small particles was found to be inconsistent in the presence of large particles, even if a low concentration of large particles existed. In order to eliminate the interferences from large particles, a special filtration process was necessary before measuring the small particle size. An attempt was made with different types as well as different pore size filters. It was concluded that filter paper (regardless of type) was not suitable for this experiment. Having experimented with other filtering processes, a disposable nylon syringe filter with 5 μm pore size was found to be suitable for the study.

Zeta Potential Measurements

Principle

The basic principles of zeta potential measurements include three different aspects. First, the velocity (V) of charged colloidal particles in liquids between the electrodes is measured by a laser Doppler shift. Second, the electrophoretic mobility (μ) is determined based on the measured velocity and the electric field strength (E) by the equation $V = \mu E$. The zeta potential (ζ) can be calculated from the solution conditions and the mobility

by the equation $\zeta = \mu\eta/\varepsilon$ where η is the viscosity of the liquid and ε is the dielectric permittivity. However, the equation is only correct for certain combination of particle size and ionic strength. Either mobility or zeta potential may be used as measures of dispersion stability although zeta potential is used more widely. The principles of zeta potential measurement are illustrated in Figure 2-7.

Measurement Procedure

A detailed testing procedure that is recommended by the manufacturer is given in Appendix B. Major steps are outlined as follows:

1. Instrument preparation.
2. Background measurement.
3. Blank sample measurement.
4. Calibration.
5. Sample preparation.
6. Clean the electrodes and insert the electrode assembly into the cell.
7. Insert the cell into the cell compartment.
8. Make a measurement.

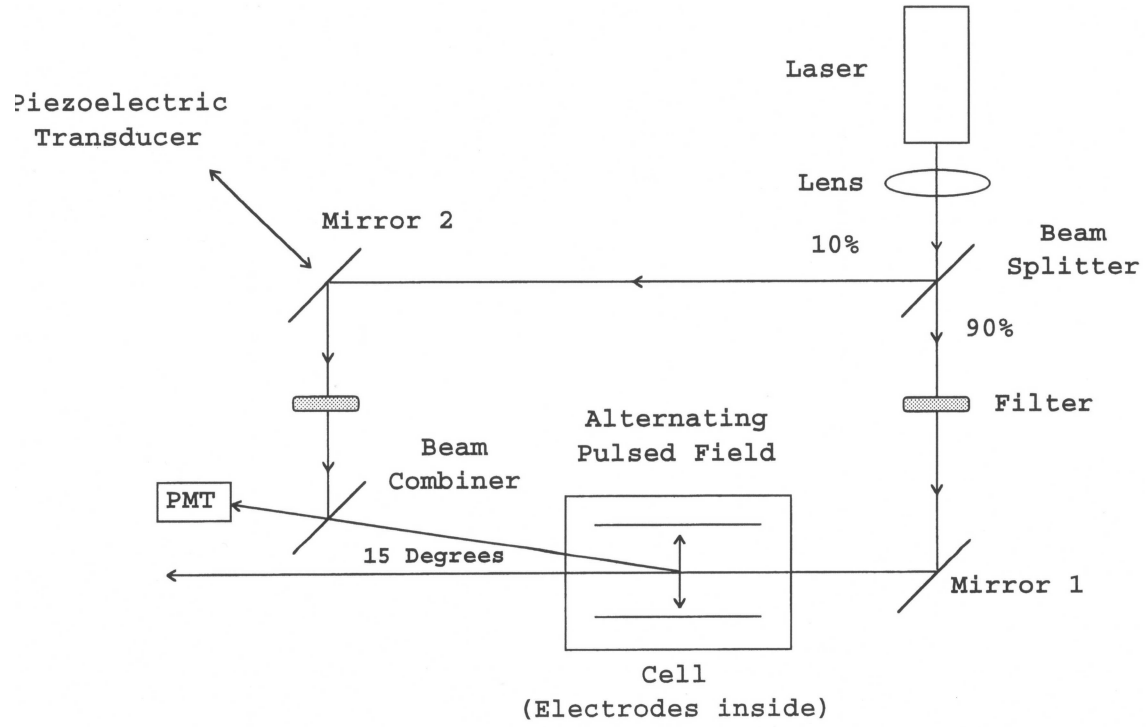

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Figure 2.7 Principles of Zeta Potential Measurement

Chapter 3
Experimental Program

3.1 Sample Preparation

Past studies have identified urban stormwater runoff as a major contributor to the degradation of many urban lakes, streams, and rivers. Industrial and commercial parking lots, material storage areas, and automobile service stations are the most significant contributors of a variety of pollutants to wet weather flow. Therefore, an attempt was made to analyze both stormwater runoff and synthetic samples. The former was intended to provide a preliminary guideline in parking lot runoff characteristics, while the latter allowed a consistent background for experimentation. Preparation and evaluation procedures for each type of sample are described in this section. In addition, CSO samples were also used for this study.

Surface Runoff

During the initial stage of the investigation, surface runoff samples were collected from a parking lot. In addition to natural storm surface runoff samples, simulated runoff was generated by spraying the above-noted parking lot with city water during dry weather periods.

The parking lot used in this study was the Otto H. York Center Parking Lot #3 at the New Jersey Institute of Technology (NJIT) campus in Newark, New Jersey. The parking lot has a capacity of 60 cars with a dimension of approximately 100 meters by 30 meters with a 4% grade. It operates seven days per week with five days at full capacity.

Sampling of actual stormwater runoff events is weather dependent, and hydrologic factors such as the interval between storm events, rainfall intensity, total rainfall, etc. are random in nature, and, as such, greatly affect runoff characteristics. Because of this, the time to conduct the experiments and the ability to replicate results with varying samples would have required a substantially longer period than is programmed in the investigation. Therefore, actual runoff samples were used only in the preliminary stage of this study to test the feasibility of the MC process.

Sampling.
Bulk runoff samples generated by natural rain or by spraying a predetermined area of the parking lot with city water were sampled at the beginning of the precipitation event directly from the drainage inlet chamber by a hand-bucket and industrial vacuum apparatus. The pavement was washed from the highest elevation to the lowest elevation. The total area washed for each of the

tests was approximately 3,000 square feet. Sampling setup and operations were prepared at least two days prior to rainfall events anticipated in accordance with the weather forecast.

Sample Preservation, Transportation, and Storage.
Samples were transported to the laboratory within five minutes after finishing the sample collection process. The preservation and holding time of samples are listed in Table 3-1.

Table 3-1. Preservation Condition and Holding Time For Sample Analysis

Parameter	Container	Preservation	Holding Time
Particle size distribution	P, G*	Cool, 4°C	48 hours**
Zeta potential	P, G	Cool, 4°C	48 hours**
Suspended solid	P, G	Cool, 4°C	7 days
Total solid	P, G	Cool, 4°C	7 days
Volatile solids	P, G	Cool, 4°C	7 days
pH	P, G	None	Immediately
Fecal coliform	P, G	Cool, 4°C	6 hours
Total organic carbon	P, G	Cool, 4°C	28 days
Turbidity	P, G	Cool, 4°C	48 hours

* P -- plastic container; G -- glass bottle
** No standard holding time is given in the currently available literature. This number is selected based on turbidity holding time.

Synthetic Samples.
As indicated above, evaluation of the MC process by both natural and simulated runoff requires a substantial amount of sampling due to the randomness of runoff samples. Since the dry residual materials from a parking facility also possess the basic constituents of parking lot runoff, such residues were collected

and used to prepare synthetic samples. It was found that two types of dry materials existed:

Type I -- Low organic content materials. The type I material is a low organic content sandy-like residue that was found in the area along the walls of the parking deck. The total volatile solid content of this type of material was found to be less than 1% by weight. This material was sieved and divided into the seven particle size ranges as shown in Table 3-2.

A series of sample preparation evaluation tests were conducted to determine the quantity of each range for the aqueous sample to be analyzed. It was found that the material with grain size larger than 106 μm would settle too fast to make a uniform sample. It was concluded that particles smaller than 106 μm were more suitable for suspension than the larger particles. Subsequently, particles smaller than 106 μm were used to prepare synthetic samples. The constituents of the synthetic samples are illustrated in Table 3-3.

Table 3-2. Dry Sample Size Characteristics

Particle Diameter (μm)	Control Sieve No. (ASTM)
less than 53	270
53 — 75	270 — 200
75 — 106	200 — 140
106 — 150	140 — 100
150 — 250	100 — 60
250 — 425	60 — 40
larger than 425	40

Table 3-3. Composition of Synthetic Samples

Material Type	Specification	Relative Weight*	Remarks
Type I Low organic content material	size < 53 (μm)	38.9%	By sieve analysis
	53 < size < 75 (μm)	19.4%	
	75 < size < 106 (μm)	8.3%	
Type II with Clay	High organic content	1.9%	High organic content materials were ground with clay
	0.1 < size < 3 (μm)	31.4%	
Total		100%	

* based on the total weight of dry sample

Type II -- High organic content material. The type II material is a high organic content residue that was attached to the ground surface under each parked car. The total volatile solids for this type of material were found to be approximately 18% by weight. In performing sample preparation tests, it was observed that this material either settles at the bottom of the jar or floats on the surface. In order to obtain suspended volatile solids, the high organic content material was first ground with clay and then used to prepare an aqueous sample. After grinding with clay, it was observed that the type II solids remained in a suspended state, which was confirmed by total volatile solid testing. A series of tests were conducted to determine the proportion between clay and the original sample. Both low and high organic content materials were combined and used to generate a synthetic sample. The composition of the type II material ground with clay is shown in Table 3-3.

Combined Sewer Overflow

The City of Perth Amboy operates a combined sewer system and wastewater transfer pumping station that collects combined sanitary sewage, industrial wastewater, and storm runoff from an approximately 7 square kilometers drainage area to a regional wastewater treatment plant owned and operated by the Middlesex County Utilities Authority. The wastewater transfer pumping facility is located at the junction of Water Street and Sadowski Parkway. A CSO regulator is directly located about 20 feet below the Sadowski Parkway with an overflow weir and 84" diameter CSO tide-gated outfall to the Arthur Kill.

The inflow from the interceptor discharges into one of two screening channels each equipped with a mechanics coarse bar screen for removing screenings and protecting the sewage pumps. The screen chamber inflow was collected for the MC coagulation study.

The channel is housed in an enclosed building with 24 hours a day access and a person always on duty. Grit, that accumulates in the channel, is removed from the facility monthly.

3.2 Measurement Parameters

In this experimental program, the parameters were divided into control and response variables.

Control Variables

Control variables are independent variables of a system whereas response variables are dependent variables (results). In this study, the control variables included the following parameters:

- MC type, size range, and concentration.
- Coagulant type and concentration.
- Coagulant aid (coagulant aid) type and concentration.
- Rapid mixing time and rotation rate.
- Slow mixing (flocculation) time and rotation rate.

Response Variables

Response variables are indicators used for determining the effectiveness of the control variables. Response variables may provide useful information in determining the optimal setup for control variables. In this study, the following parameters were used as response variables:

- Supernatant turbidity.
- Supernatant pH.
- Supernatant particle-size-distributions.
- Supernatant zeta potential.
- Supernatant suspended solids.
- Supernatant total solids.
- Supernatant volatile solids.
- Supernatant fecal coliform.
- Supernatant total organic carbon.

Raw Stormwater Characterization. The raw samples including surface runoff, synthetic samples, and CSO (see Section 3.1) were characterized by the following parameters:

pH	Total volatile solids
Turbidity	Zeta potential
Total solids	Total organic carbon
Particle size distribution	Fecal coliform
Suspended solids	

3.3 Experimental Design

The experimental design of this study consisted of a three-layer experimental design: prescreening tests, screening tests, and confirmative tests. The purpose of the prescreening tests during which different experimental conditions were evaluated by visual observation was to determine the range of operational parameters. Upon the completion of the prescreening tests, screening tests were performed followed by confirmative tests. The purpose of screening and confirmative tests was to provide a quantitative analysis of the MC process. Detailed descriptions of MC, coagulant, coagulant aid, prescreening tests, screening tests, and confirmative tests are given in the following sections.

Microcarrier (MC)

Two types of material were selected to use as MC, namely, Ottawa sand and a beach sand obtained from Sandy Hook, NJ. Both sands were used in prescreening tests. Ottawa sand was selected in screening and confirmative testing, due to its durability and size uniformity over the Sandy Hook beach sand and commercial available in large quantity. The size range of Ottawa sand tested was between 100 to 500 μm. The MC size ranges and concentrations were determined by prescreening tests.

All containers and MC were first washed thoroughly with a detergent and hot water, then rinsed with hot water to remove all traces of residual washing compound, and finally rinsed with particle-free water.

Coagulant

Alum (aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$)and ferric chloride ($FeCl_3 \cdot 6H_2O$) were used as the coagulants for this study. Aluminum sulfate has been employed extensively in water and wastewater treatment because it is usually less expensive than other coagulants and it operates effectively close to neutral pH's while ferric chloride is effective over a wider pH range. Concentrations of coagulant reported in this report are the concentration of aluminum sulfate as mg of $Al_2(SO_4)_3 \cdot 18H_2O$/L and the concentration of ferric chloride as mg of Fe^{+++}/L.

The zeta potential and pH of aluminum sulfate and ferric chloride were measured at different concentrations. Stock coagulant test solutions were prepared daily by mixing chemicals with deionized water to a concentration of 10 g/L (1 mL of stock solution when added to 1 L of sample is equivalent to 10 mg/L). The zeta potential and pH values of the deionized water were close to 0 mV and 7, respectively.

The zeta potential distributions of aluminum sulfate and ferric chloride solutions for different concentrations are presented in Figures 3-1 and 3-2. The zeta potential increases with the increase of concentration within the range of 10—100 mg/L for both coagulants. For concentrations higher than 100 mg/L, no significant changes for zeta potential was noticed.

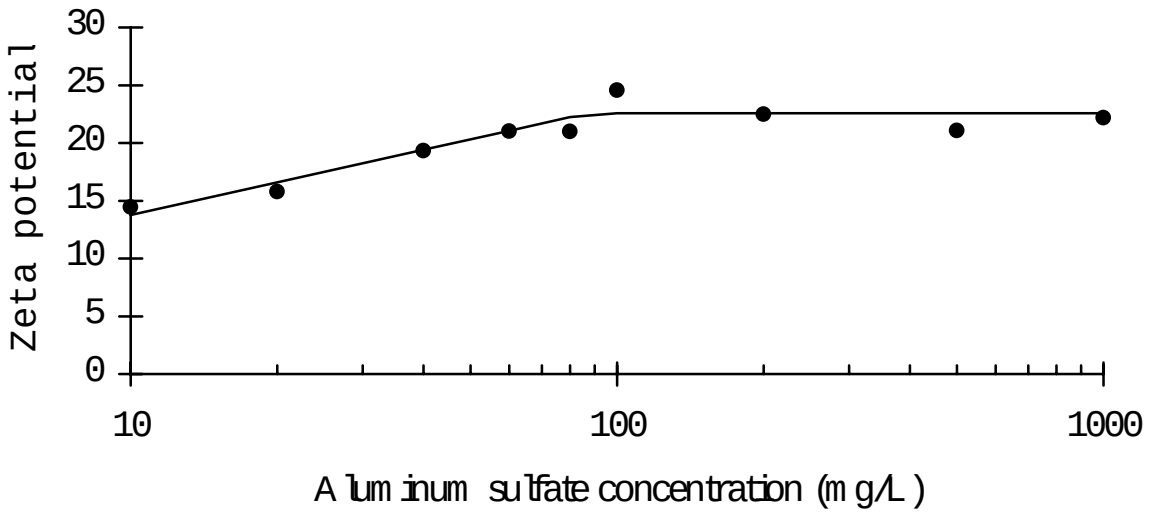


Figure 3-1. Zeta Potential Distribution of Aluminum Sulfate Solution

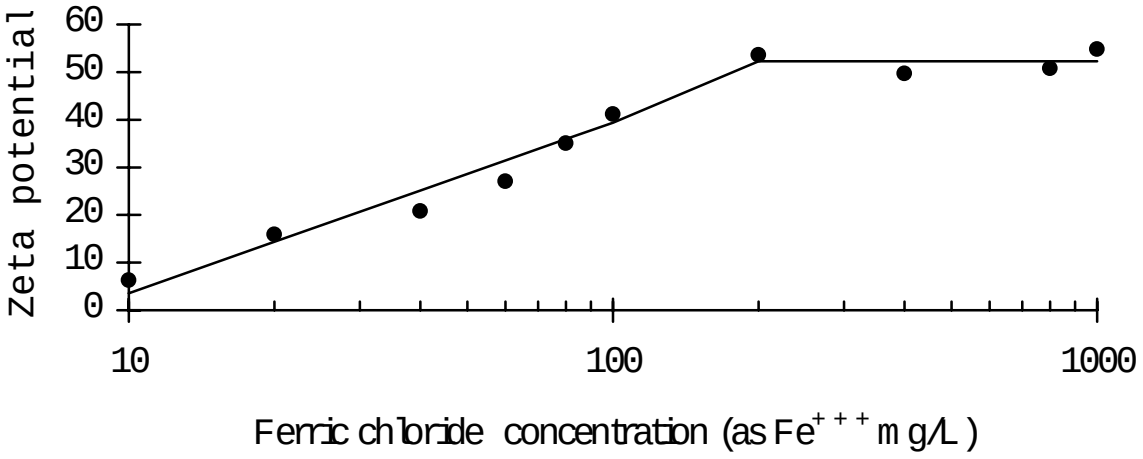


Figure 3-2. Zeta Potential Distribution of Ferric Chloride Solution

Figures 3-3 and 3-4 illustrate variation of pH values with different concentrations of coagulant. The pH value decreases from 5.2 to 3.5 for aluminum sulfate concentrations increases from 10 to 1000 mg/L as $Al_2(SO_4)_3 \cdot 18H_2O$, and the pH values vary from 3.5 to 2.3 for ferric chloride solution when the concentration of ferric chloride increases from 10 to 1000 mg/L as Fe^{+++} (or 48 to 4,800 mg/L as $FeCl_3 \cdot 6H_2O$).

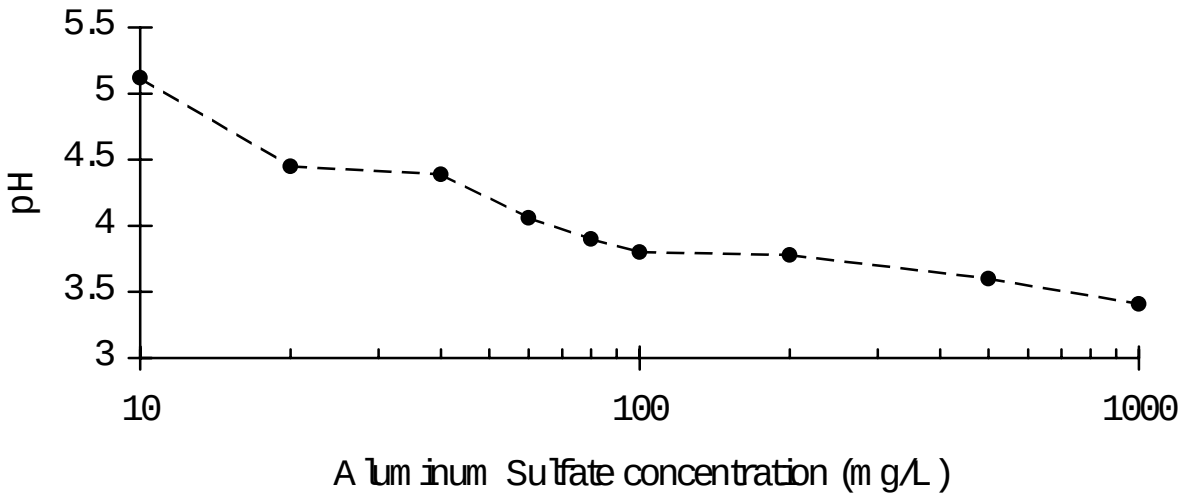


Figure 3-3. pH Distribution of Aluminum Sulfate Solution

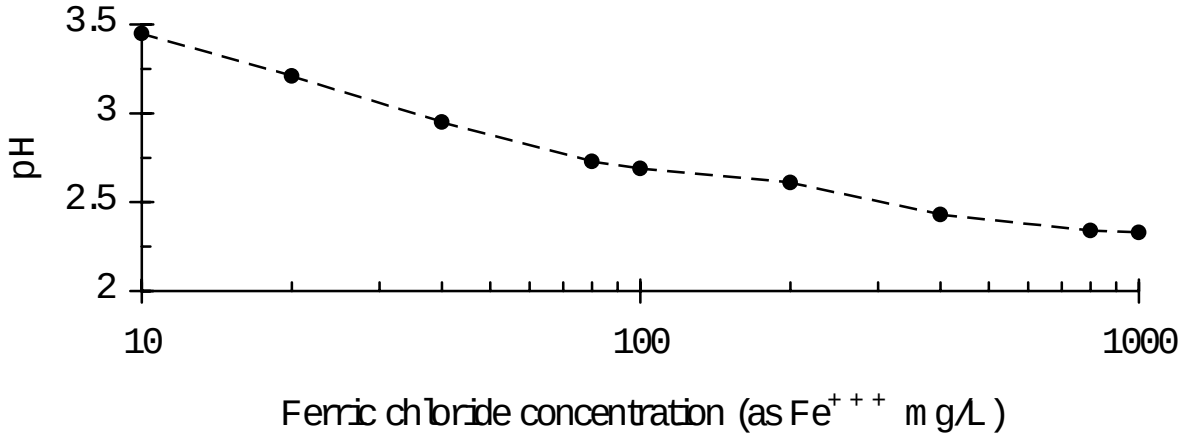


Figure 3-4. pH Distribution of Ferric Chloride Solution

Coagulant Aid

There are many commercially available coagulant aids or polyelectrolytes. Five polyelectrolytes from two different manufacturers (see Table 3-4) were used in the experiments. Among them, four (POL-EZ-2466, POL-EZ-3466, POL-EZ-2696, and POL-EZ-7736) were used in surface runoff tests and one (309C) for CSO tests. Zeta potential distributions versus polyelectrolytes concentrations are illustrated in Figures 3-5, 3-6, 3-7, and 3-8, respectively. For cationic and anionic polyeletrolytes, the charge strengths are stronger for higher concentrations, while for non-ionic polymer, there is no significant change in zeta potential when concentration increases.

The relationship between coagulant aid concentrations and zeta potential values based on log-linear regression is summarized in Table 3-5 and illustrated in Figure 3-9. One can see that the cationic (POL-EZ-2466 and POL-EZ-3466) and anionic (POL-EZ-7736) coagulant aids have similar strengths of charge while the zeta potential of the non-ionic coagulant aid (POL-EZ-2696) is comparatively insignificant.

Table 3-4. List of Coagulant Aids

Coagulant Aid (Polyelectrolyte)	ID	Charge	Test Stage	Manufacturer
POL-EZ-2466	PE-1	Cationic	Surface Runoff	Calgon Corporation Pittsburgh Pennsylvania
POL-EZ-3466	PE-2	Cationic		
POL-EZ-2696	PE-3	Non-ionic		
POL-EZ-7736	PE-4	Anionic		
309C	PE-5	Cationic	CSO	Polydyne, Inc Riceboro Georgia

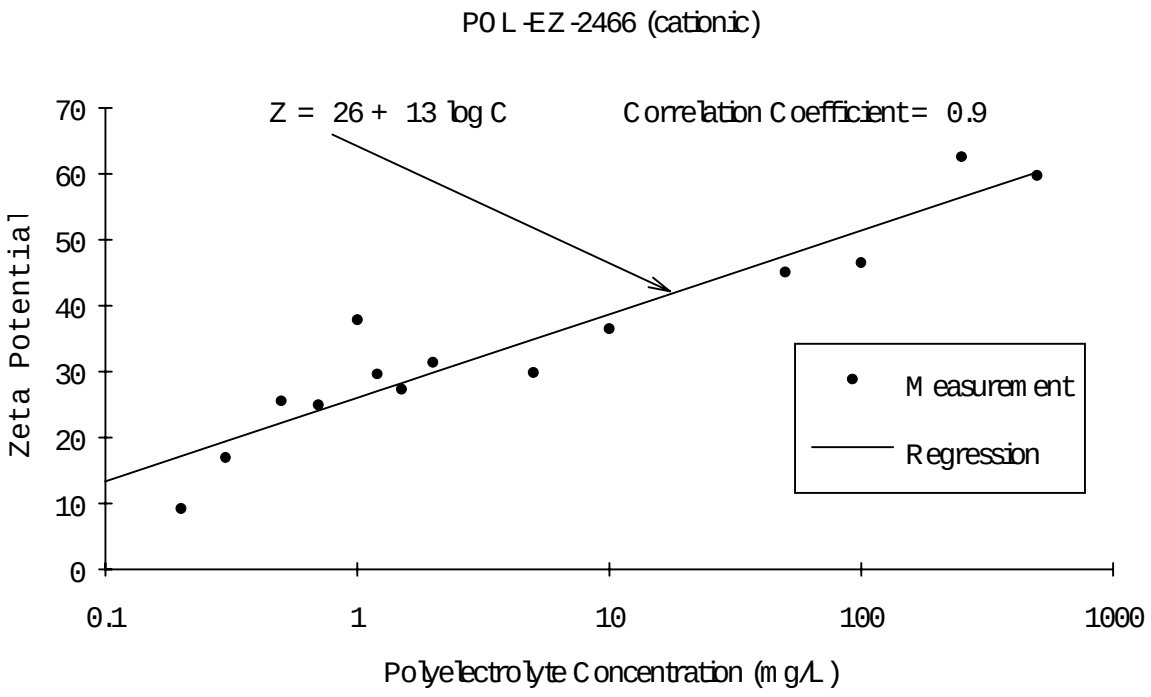


Figure 3-5. Zeta Potential Distribution of POL-EZ-2466

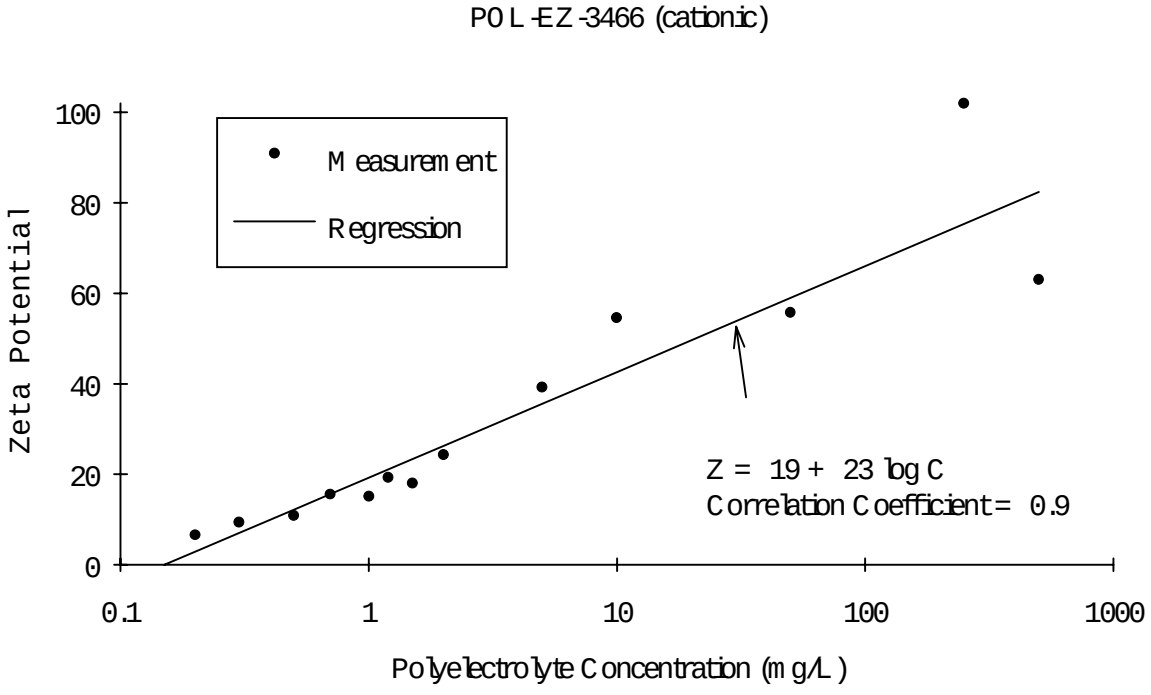


Figure 3-6. Zeta Potential Distribution of POL-EZ-3466

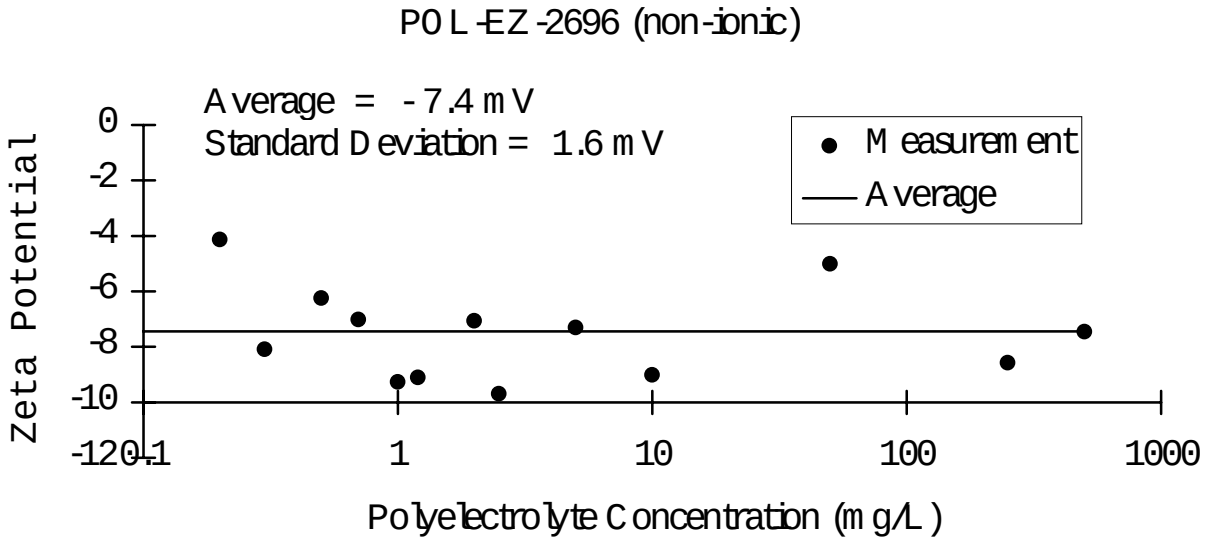


Figure 3-7. Zeta Potential Distribution of POL-EZ-2696

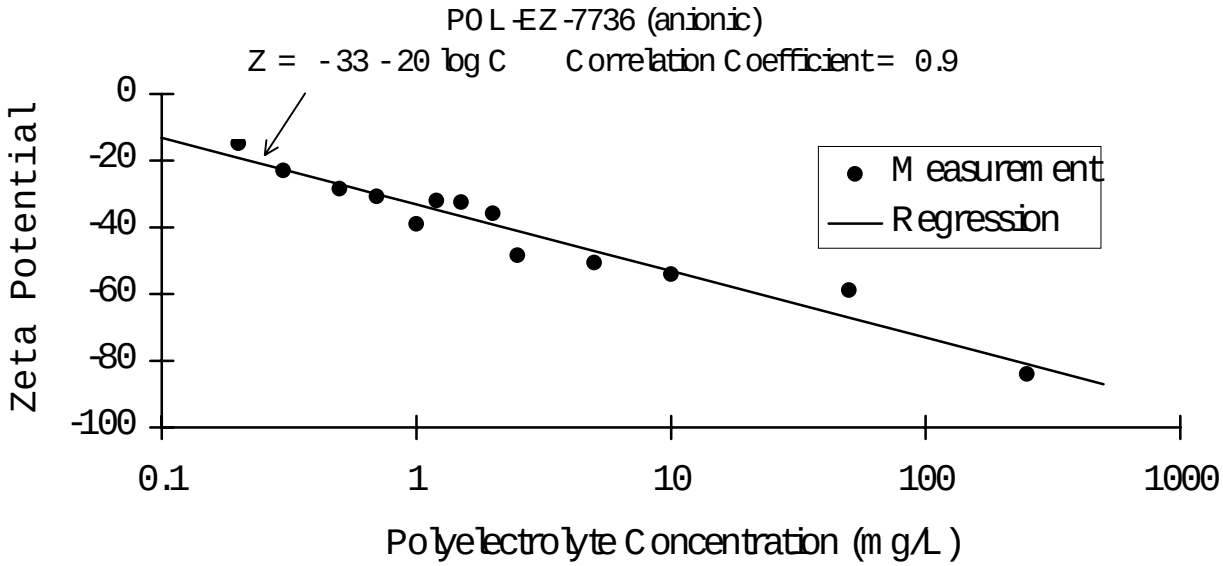


Figure 3-8. Zeta Potential Distribution of POL-EZ-7736

Table 3-5. Zeta Potential of Coagulant Aids

Coagulant aid	Zeta Potential versus Concentration
POL-EZ-2466	Z = 26 + 13 log C
POL-EZ-3466	Z = 19 + 23 log C
POL-EZ-2696	$Z_{average}$ = -7.4 Standard deviation = 1.6 mV
POL-EZ-7736	Z = - 33 - 20 log C

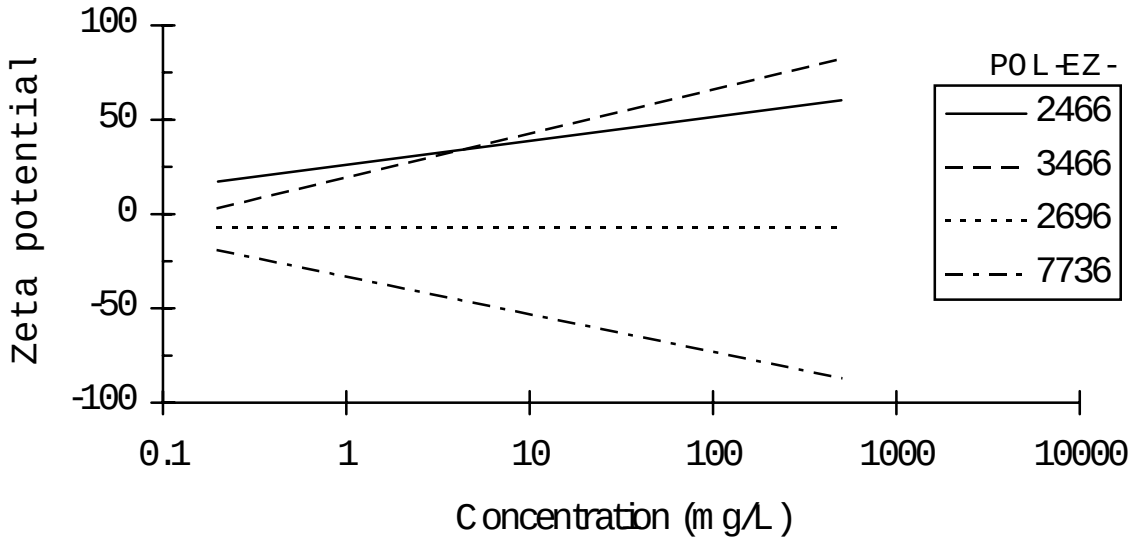


Figure 3-9. A Comparison of Zeta Potential of Coagulant Aid

Experiments

The experimental program consisted of three phases, namely, prescreening, screening, and confirmative tests. The prescreening phase was a qualitative determination that provided operational setups for the screening and confirmative tests. The screening tests evaluated various coagulant and coagulant aid concentrations for the MC jar tests. Finally, the confirmative tests assessed the effects of MC size and concentration in the jar test. The function and program of each phase is described in detail in the following sections.

Prescreening Jar Tests

The prescreening tests consisted of a qualitative characterization to provide testing ranges for the control variables (see Section 3.2). In the prescreening tests, a series of jar tests was performed on natural and artificial storm runoff samples mixed with MC, coagulant and coagulant aid. The operational parameters included: coagulant aid type and dosage, coagulant dosage, rapid mixing rate and duration, flocculation mixing rate and duration, and MC type, concentration, and size. The degree of agitation, time required for good floc formation, and the time required for settling were noted. Since the results are largely comparative, visual observation was employed. Quantitative analysis was considered unnecessary. The parameters and their ranges are listed in Table 3-6.

Table 3-6. Parameter Setup for Prescreening Jar Tests

Parameter	Material	Value Ranges
MC Size	Ottawa sand Beach sand	100—500 μm
MC Concentrations	Ottawa sand Beach sand	3—10 g/L
Coagulant	Aluminum sulfate	10—120 mg/L
Coagulant aid	POL-E-Z 3466	0.3—1.5 mg/L
Coagulant aid	POL-E-Z 2466	0.3—1.5 mg/L
Coagulant aid	POL-E-Z 7736	0.3—1.5 mg/L
Coagulant aid	POL-E-Z 2696	0.3—1.5 mg/L
Rapid Mixing Rate	————	60—200 rpm
Flocculation Rate	————	10—60 rpm
Rapid Mixing Duration	————	10—120 sec
Flocculation Duration	————	10 sec—30 min
Settling Time	————	1—30 min

The minimum energy and time that can initiate all the MC into suspension were selected as the rapid mixing rate and duration for the jar tests. In addition, the minimum rate to keep all MC in suspension was selected as the optimal flocculation rate. The optimal flocculation time was determined based on floc formation. The rapid mixing rate and duration as well as the flocculation rate and duration were determined by visual observation. A summary of parameters with respect to this criteria selection is shown in Table 3-7.

Five MC configurations with different sizes and concentrations were selected based on prescreening tests and they are identified in Table 3-8.

Table 3-7. Determination of Rapid Mixing Rate with Duration and Flocculation Rate with Duration

Parameter	Selection Criterion
Rapid mixing rate	Minimum energy to initiate MC into the suspension
Rapid mixing duration	Minimum time to achieve fully mixed condition
Flocculation rate	Minimum energy to keep all MC and floc in the suspension
Flocculation duration	Best floc formation (size and density) at observation intervals of 1, 3, 5, 10, 15, 20, and 30 min

Screening Tests

The screening tests focused on determining the optimal doses of coagulant and coagulant aid for the MC process. There were three test levels with different combinations of MC, coagulant and coagulant aid. A summary of parameter evaluation for screening as well as confirmative tests is presented in Table 3-9.

Table 3-8. MC Identification

MC type	Material	Size	Dosage (g/L)
MC-1	Ottawa sand	53—150 µm (Sieve #270—#100)	3
MC-2	Ottawa sand	150—250 µm (Sieve #100—#60)	3
MC-3	Ottawa sand	53—150 µm (Sieve #270—#100)	10
MC-4	Ottawa sand	150—250 µm (Sieve #100—#60)	10
MC-5	Ottawa sand	53—75 µm (Sieve #270—#200)	3

Table 3-9. Screening and Confirmative Tests Parameter Evaluation

Test	Parameter	Control Variable
Screen level 1	MC-1 and Coagulant	Coagulant concentration
Screen level 2	MC-1, Coagulant, and Coagulant aid	Coagulant concentration
Screen level 3	MC-1, Coagulant, and Coagulant aid	Coagulant aid concentration
Confirmative	MC-1, MC-2, MC-3, MC-4, Coagulant, and Coagulant aid	MC size MC concentration

Rate and duration for rapid mixing and flocculation determined in prescreening tests were used for the screening tests. Turbidity was used as a water quality indicator. Supernatant samples were taken at settling times of 3 and 8 minutes, respectively.

Determination of optimal dose was based on the following criteria:

- Select the jar with the lowest turbidity, unless
- The difference between the lowest turbidity jars is less than 20%, in which case, select the jar with the lower chemical dosage.

Level 1. The purpose of Level 1 testing was to determine the best coagulant dosage in the absence of coagulant aid. MC-I was used for each jar. Coagulant concentration setup, ranging from 0 to 80 mg/L, is illustrated in Table 3-10.

Table 3-10. Screening Tests -- Level 1

Test Set	Additive	Jar No.					
		1	2	3	4	5	6
1-1	MC	M C - 1					
	Coagulant (mg/L)	0	10	20	40	60	80

Level 2. The purpose of level 2 testing was to determine the best coagulant dosage in the presence of coagulant aid. The influence of coagulant aid on the optimal dosage of coagulant was thus determined. Coagulant, MC-I, and 1 mg/L coagulant aid were used in the tests. The coagulant concentration setup, ranging from 0 to 80 mg/L, is illustrated in Table 3-11.

Level 3. The purpose of level 3 testing was to determine the influence of coagulant aid concentrations. The optimal coagulant concentration based on the test results of level 2, and MC-I was used for each jar. The coagulant aid concentration setup, ranging from 0.3 to 1.5 mg/L, is presented in Table 3-12.

Table 3-11. Screening Tests -- Level 2

Test Set	Additive	Jar No.					
		1	2	3	4	5	6
2-1	MC	M C - 1					
	Coagulant (mg/L)	0	10	20	40	60	80
	Coagulant aid PE-1 (mg/L)	1	1	1	1	1	1
2-2	MC	M C - 1					
	Coagulant (mg/L)	0	10	20	40	60	80
	Coagulant aid PE-2 (mg/L)	1	1	1	1	1	1
2-3	MC	M C - 1					
	Coagulant (mg/L)	0	10	20	40	60	80
	Coagulant aid PE-3 (mg/L)	1	1	1	1	1	1
2-4	MC	M C - 1					
	Coagulant (mg/L)	0	10	20	40	60	80
	Coagulant aid PE-4(mg/L)	1	1	1	1	1	1

Table 3-12. Screening Tests -- Level 3

Test Set	Additive	Jar No.					
		1	2	3	4	5	6
3-1	MC	M C - 1					
	Coagulant (mg/L)	based on results from test set 2-1					
	Coagulant aid PE-1 (mg/L)	1	0.3	0.5	0.7	1.2	1.5
3-2	MC	M C - 1					
	Coagulant (mg/L)	based on results from test set 2-2					
	Coagulant aid PE-2 (mg/L)	1	0.3	0.5	0.7	1.2	1.5
3-3	MC	M C - 1					
	Coagulant (mg/L)	based on results from test set 2-3					
	Coagulant aid PE-3 (mg/L)	1	0.3	0.5	0.7	1.2	1.5
3-4	MC	M C - 1					
	Coagulant (mg/L)	based on results from test set 2-4					
	Coagulant aid PE-4 (mg/L)	1	0.3	0.5	0.7	1.2	1.5

Confirmative Tests

In confirmative tests, it was intended to determine the impact of the MCs with respect to their size and concentration. In these tests, one coagulant, four MCs, and four coagulant aids were used. The experimental setup is outlined in Table 3-13.

Table 3-13. Confirmative Tests

Test Set	Additive	Jar No.				
		1	2	3	4	5
C-1	MC	M C - 1				
	Coagulant (mg/L) and Coagulant aid (mg/L)	Based on Test Set 1-1	Based on Test Set 3-1	Based on Test Set 3-2	Based on Test Set 3-3	Based on Test Set 3-4
C-2	MC	M C - 2				
	Coagulant (mg/L) and Coagulant aid (mg/L)	Based on Test Set 1-1	Based on Test Set 3-1	Based on Test Set 3-2	Based on Test Set 3-3	Based on Test Set 3-4
C-3	MC	M C - 3				
	Coagulant (mg/L) and Coagulant aid (mg/L)	Based on Test Set 1-1	Based on Test Set 3-1	Based on Test Set 3-2	Based on Test Set 3-3	Based on Test Set 3-4
C-4	MC	M C - 4				
	Coagulant (mg/L) and Coagulant aid (mg/L)	Based on Test Set 1-1	Based on Test Set 3-1	Based on Test Set 3-2	Based on Test Set 3-3	Based on Test Set 3-4

Chapter 4
Experimental Results: Surface Runoff

4.1 Prescreening Tests

The function of the prescreening tests was to determine the ranges of operational parameters to be utilized in the study for the control variables employed. As stated in Chapter 3, E-1 and E-2 represent aluminum sulfate and ferric chloride, respectively. Names and identifications of coagulant aids and MCs are indicated in Tables 3-4 and 3-8, respectively. A series of jar tests was performed with conditions stated in Table 3-7.

Rapid mixing. Based on the prescreening trials, two stages of rapid mixing were used in the MC weighted jar tests. In the first stage, a mixing rate of 150 rpm for 10 seconds was required to lift MCs from the bottom of the jar into suspension. In the second stage, a mixing rate of 100 rpm was required to keep the MC in suspension. It was observed that floc growth began 10 seconds from the beginning of the second rapid mixing stage. Floc shear would occur due to the rapid speed if the rapid mixing rate of 100 rpm were continued. Based on this observation, a 10-second duration was selected in the second stage of rapid mixing.

Slow mixing (flocculation). It was observed that both MC and flocs would settle without further flocculation if the slow mixing rate were lower than 60 rpm. 60 rpm was found to be an appropriate mixing rate to avoid floc shear but still keep MCs and flocs in suspension. A 10-second duration was found to be sufficient for the flocculation process.

In the MC weighted jar test, the total mixing time (approximately 30 seconds) is much shorter than those used in conventional jar tests. This indicates that MC might be an effective approach in reducing the treatment time and in turn, the treatment cost, compared to conventional coagulation processes. Due to the presence of MCs, however, both rapid and flocculation mixing rates of MC weighted jar tests were higher than those of conventional jar tests.

In addition, it was observed that the supernatant was rather clear after 3 minutes of settling. As a result, 3 and 8 minute sampling times were selected to study the settling kinetics.

Table 4-1 is a summary of experimental settings based on prescreening tests. These settings were used as operating conditions for both screening and confirmative tests.

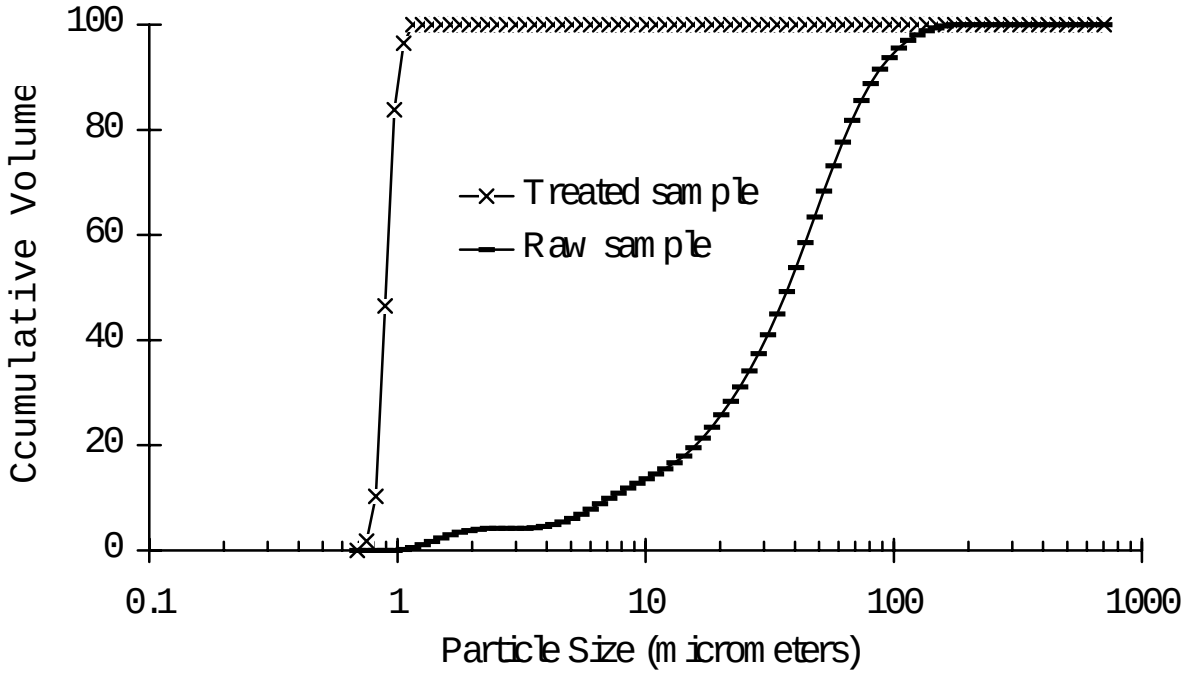
Table 4-1. Summary of Experimental Settings

Parameter	Value
Rapid mixing rate -- stage-1	150 rpm
Rapid mixing duration -- stage-1	10 sec
Rapid mixing rate -- stage-2	100 rpm
Rapid mixing duration -- stage-2	10 sec
Slow mixing (Flocculation) rate	60 rpm
Slow mixing duration	10 sec
MC concentration -- 1	3 g/L
MC concentration -- 2	10 g/L
MC size -- 1	53—150 μm
MC size -- 2	150—250 μm
Settling time -- 1	3 min
Settling time -- 2	8 min
Coagulant concentration	10—80 mg/L
Coagulant aid concentration	0.3—1.5 mg/L

4.2 Effects of MC Coagulation

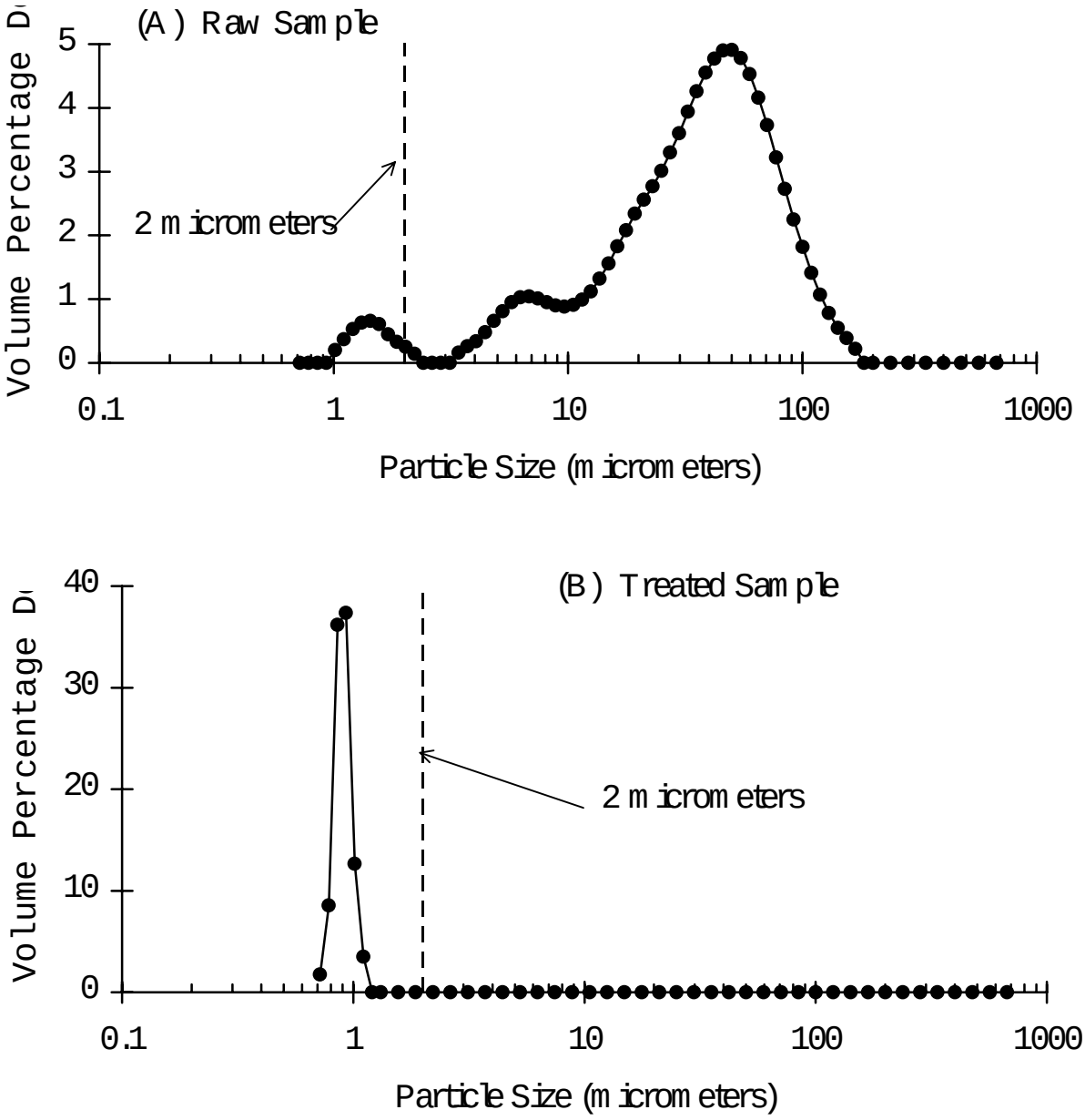
Figure 4-1 illustrates cumulative volume distributions versus particle size before and after the MC weighted coagulation. For the raw sample (before treatment), the measurable range of particle size is from 1 to 170 μm which consists of 81% from 10 to 100 μm and 14% smaller than 10 μm. After the MC coagulation, the particles in the supernatant of the jar were found to be < 2 μm, which indicated that all particles > 2 μm were removed.

Figures 4-2 (A) and (B) illustrate the particle size distribution characteristics of the raw sample and supernatant sample after treatment, respectively. For the raw sample, the distribution peak is at approximate 50 μm while the small particles (from 0.7 to 2 μm) were either undetectable or only a low percentage compared to the peak.



MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L
E-1: Aluminum Sulfate Concentration = 40 mg/L
PE-1: Polyelectrolyte POL-EZ-2466 Concentration = 1 mg/L

Figure 4-1. Particle Sizes of Raw and Treated Samples (Cumulative)



MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L
E-1: Aluminum Sulfate Concentration = 40 mg/L
PE-1: Polyelectrolyte POL-EZ-2466 Concentration = 1 mg/L

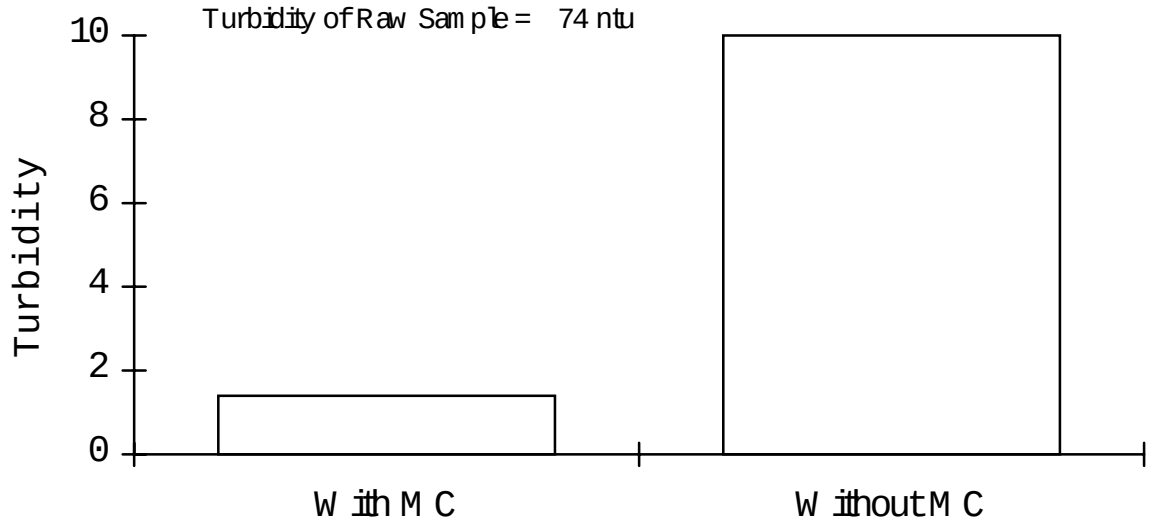
Figure 4-2. Particle Sizes of Raw and Treated Samples (Distributions)

After the treatment, only particles smaller than 2 μm were found to remain in the supernatant of the sample. Since the larger particles were all removed from the sample, the percentage of small particles increases. A summary of particle size distributions in different ranges is shown in Table 4-2. One can see that more than 96% (> 2 μm) of particles were removed from the raw sample. The removal efficiency for the 4% smaller particles (< 2 μm) was indicated by the particle count rate discussed below.

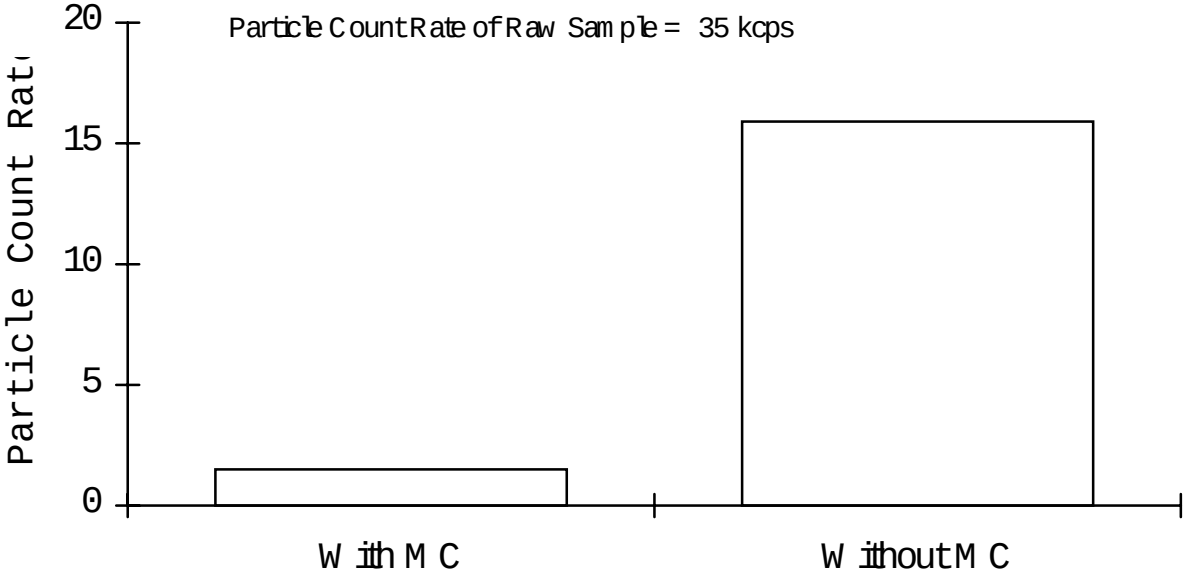
Figures 4-3 (A) and (B) present comparisons of turbidity and particle count rate (PCR) results with and without using an MC for different coagulant aids. Turbidity has been used extensively as a water quality indicator in water and wastewater treatment process analysis. The count rate, utilizing a unit of kilo-count per second, is directly related to the particle concentration in the solution; therefore, it is a good indicator for colloidal particles (containing particles smaller than 0.45 micrometer) for which TSS measurement is usually not applicable. Both turbidity and particle count rate of supernatant samples with MC are much lower than those without MC. It is apparent that the addition of MC improves the treatment process effectively.

Table 4-2. Particle Size Distribution of Raw and Treated Samples

Size Range (μm)		0.69—1	1—2	2—10	10—100	100—170
Volume (%)	Raw	< 0.1	4	10	81	5
	Treated	84	16	< 0.1	< 0.1	< 0.1



(A) PE-4 (Anionic)



(B) PE-3 (Non-ionic)

MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L
E-1: Aluminum Sulfate Concentration = 40 mg/L
PE-3: Polyelectrolyte POL-EZ-2696 Concentration = 1 mg/L
PE-4: Polyelectrolyte POL-EZ-7736 Concentration = 1 mg/L

Figure 4-3. Effectiveness of the MC Process

4.3 Screening Tests

For each test set, supernatant samples were taken at 3 minute and 8 minute settling times, respectively. The time difference for sampling six jars was less than 15 seconds, which was negligible.

Screening tests include three levels of setup conditions that are summarized in Tables 3-10 through 3-12 (Section 3.3). Results of these three levels of tests are described in the following sections.

Level One

In this level, only an MC and a coagulant were used for the treatment process. The concentration of coagulant range from 0 to 80 mg/L (see Table 3-10).

pH

Figure 4-4 illustrates the relationship of pH and coagulant concentration. It is seen that pH decreases as coagulant concentration increases. All pH values are in the range of 6.5 to 7.5 except for jar number six with 80 mg/L coagulant. For coagulant concentration between 20 and 80 mg/L, pH values with 8 minute settling time are closer to neutral than those with 3 minute settling time. The changes of pH values may be due to that some of the immediate pH drop (as aluminum hydroxide is formed from alum) is counteracted by a slow loss of carbon dioxide to the atmosphere, raising the pH slowly.

Turbidity

Figure 4-5 shows the turbidity distribution versus coagulant concentration. Here the lowest turbidity for both 3 and 8 minute settling times was found at 60 mg/L. In addition, the 8-minute settling time yields better results (lower turbidity) than the 3 minute settling time.

Zeta Potential

Figure 4-6 illustrates zeta potential values versus coagulant concentrations. It can be seen that the zeta potential basically increases as coagulant concentration increases. At coagulant concentrations between 60 and 80 mg/L, the differential of zeta potential becomes greater between settling times of 3 minutes and 8 minutes.

Turbidity versus Zeta Potential

It is of interest to see the correlation between zeta potential and turbidity presented in Figure 4-7. The turbidity decreases for less charge in the zeta potential range of -10 to -25 mV. A log-linear regression was performed based on measurements within the negative zeta potential range. The straight line in the positive zeta potential side is the imaging line of the negative

side. Since there is only one point on the positive side, regression at this side is impossible. Generally, organic colloids require zeta potentials near zero for optimal coagulation, while clay-related turbidity is best removed at slightly negative zeta potentials. In this case, the fact that the measured point is very close to the image line indicates that the zero potential is the image symmetrical point, and so, is the best for turbidity removal.

Particle Count Rate

The particle count rate for 60 mg/L coagulant was found to be 1.2 and 1.0 at settling times of 3 minutes and 8 minutes, respectively (see Figure 4-8). Results showed that approximately 50% of the small particles (< 5 μm) were removed from the raw sample in 3 minutes.

Level Two

Level two parameters include MC, coagulant, and four types of coagulant aids with a fixed concentration of 1 mg/L. For each coagulant aid, coagulant concentration was varied from 0 to 80 mg/L (see Table 3-11).

pH

Figure 4-9 shows a typical pH distribution versus coagulant concentration. It appears that the relationship between pH and coagulant for both level one and level two tests is similar. A summary of pH behavior for the four coagulant aids at two different settling times (3 and 8 minutes) is shown in Figure 4-10. pH values were found to be close to 7 when coagulant concentrations were in the range of 20 to 40 mg/L.

Turbidity

The lowest value of turbidity was obtained at 40 mg/L coagulant as shown in Figure 4-11. A plot of turbidity distributions (with 3 and 8 minute settling times) versus coagulant concentration with the four coagulant aids is illustrated in Figure 4-12. Based on the turbidity results, the optimal coagulant concentration for level two was 40 mg/L for all four coagulant aids. It was indicated that turbidity with 8 minute settling time is lower than that with 3 minute settling time. This is true because the longer the settling time, the more the particles will be removed.

Total Solids and Total Volatile Solids

Figure 4-13 and Figure 4-14 illustrate the total solids and total volatile solids distributions, respectively. It can be seen that 8 minutes settling time yields better results for both total solids and total volatile solids. The total solids results demonstrate that 40 mg/L was the optimal coagulant concentration.

For total volatile solids results, the optimal coagulant concentration was between 20 and 40 mg/L. Similar results were obtained for the total solids and total volatile solids removals.

Particle Count Rate

Figure 4-15 illustrates a comparison between particle count rate and turbidity. It can be seen that a similar trend indicates 40 mg/L of coagulant as the optimal concentration for turbidity and particle count rate removal.

Turbidity versus Zeta Potential

Figure 4-16 illustrates zeta potential distributions versus coagulant concentrations. Since anionic coagulant aid was added into the mixture, all supernatant samples, with the exception of 80 mg/L of coagulant samples, have larger negative charge than the raw sample. Figure 4-17 shows the correlation between turbidity and zeta potential by using a log-linear regression based on the negative zeta potential data. In addition, an image line was drawn for the positive zeta potential side with respect to the image centerline of - 10 mV zeta potential (Z). Similar to level one, it can be seen that turbidity decreases with lower zeta potential.

Level Three

In level three, four coagulant aids with concentration ranging from 0.3 to 1.5 mg/L were tested with MC-I and 40 mg/L coagulant which was determined in level two tests to be the optimal dosage for all four coagulant aids.

pH

Figure 4-18 shows the pH value versus coagulant aid concentration for the four coagulant aids at 3 and 8 minute settling times. Results indicate that coagulant aid concentration had no major influences on pH values.

Turbidity and/versus Zeta Potential

Based on the test results, the trends of turbidity removal are different for various types of coagulant aids. Figure 4-19 reveals that turbidity decreases as coagulant aid (POL-EZ-2696) concentration increases up to 1 mg/L, but varies between 1 mg/L to 1.5 mg/L. In this test set, 1 mg/L is considered as the best coagulant aid dosage. Similar observations can be found from zeta potential distributions (see Figure 4-20). By comparing the above two figures, one can see that there exists a mirror image phenomenon. As a result, a correlation between turbidity and zeta potential in the presence of coagulant aid can be established. Figure 4-21 shows the correlation of zeta potential with turbidity. The results show that the turbidity decreases for less negative charge in the range between -25 and -8 mV.

Figure 4-22 shows that turbidity decreases as coagulant aid (POL-EZ-2466) concentration increases up to 1.2 mg/L and reaches its lowest point between 0.7 and 1.2 mg/L. Figure 4-23 shows zeta potential distributions. Again, the mirror image phenomenon can be observed from these two figures. The correlation between zeta potential and turbidity is presented in Figure 4-24. It can be seen that in the zeta potential range of -3 to -15 mV, turbidity has no significant change while in the zeta potential range of -15 to -22 mV, turbidity decreases as zeta potential approach less negative charge. For other coagulant aids, the results are summarized in Table 4-3.

Particle Count Rate, Total Solids and Total Volatile Solids

Particle count rate distribution versus coagulant aid concentration is illustrated in Figure 4-25. At this point, no definite conclusion can be drawn as a result of the twin peaks. Similar trends were observed in total solids and total volatile solids versus coagulant aid concentration as shown in Figures 4-26 and 4-27, respectively. Therefore, there appears to be a functional relationship among particle count rate, total solids, and total volatile solids.

Summary

Based on the screening test results, the coagulant concentrations of 60 mg/L without coagulant aid and 40 mg/L with 1 mg/L of coagulant aid yielded better turbidity reduction efficiency. Relationships between turbidity and zeta potential under different conditions are listed in Table 4-3. For level one with coagulant in the absence of coagulant aid, the lowest turbidity point (symmetrical point) is at zero potential. For level two with additions of both coagulant (various concentrations) and coagulant aid (constant concentration), the lowest turbidity point shifted from zero potential to the range of -10 to +10 mV. For level three, for all four coagulant aids with various concentrations, the relationships between turbidity and zeta potential are either monotonously increasing (for anionic POL-EZ-7736) or decreasing (for cationic POL-EZ-2466, POL-EZ-3466 and non-ionic POL-EZ-2696).

Table 4-3. Relationship of Turbidity and Zeta Potential

Condition	Correlation Equation
Level 1	**Coagulant concentrations: 10—80 mg/L Without Coagulant aid**
log T = - 1 - 0.1 Z (- 25 < Z < 0) log T = - 1 + 0.1 Z (0 < Z < 15)	
Level 2	**Coagulant concentration: 10—80 mg/L Four coagulant aids (concentration = 1 mg/L)**
PE-1	log T = - 0.87 - 0.08 (- 25 < Z < - 6) log T = - 0.38 (- 6 < Z < 15)
PE-2	log T = 0.87 - 0.02 Z (- 25 < Z < 10) log T = 0.19 + 0.038 Z (10 < Z < 15)
PE-3	log T = - 0.9 - 0.1(Z+7) (- 25 < Z < - 7) log T = - 0.9 + 0.1(Z+7) (- 7 < Z < 10)
PE-4	log T = - 0.5 - 0.08(Z+10) (- 30 < Z < - 10) log T = - 0.5 + 0.08(Z+10) (- 10 < Z < 10)

Level 3	**Coagulant concentration = 40 mg/L Four coagulant aids (concentrations: 0.3—1.5 mg/L)**
PE-1	log T = 0.89 - 0.02 Z (-22 < Z < - 3)
PE-2	log T = 0.79 - 0.007 Z (-20 < Z < 30)
PE-3	log T = 0.33 - 0.02 Z (-25 < Z < - 8)
PE-4	log T = 1.5 + 0.05 Z (-25 < Z < -10)

Note:
T = Turbidity (ntu); Z = Zeta potential (mV)

4.4 Confirmative Tests

Based on the results from screening tests, confirmative tests were conducted to examine the influence of MC size and concentration on the MC process. Two MC size ranges,(53—150 μm defined as small MCs and 150—250 μm as large MCs) and two MC concentrations (3 g/L as low concentration and 10 g/L as high concentration) were tested. Coagulant and coagulant aid concentrations of 40 mg/L and 1 mg/L were used, respectively, for each jar test set.

MC-1 versus MC-3 and MC-2 versus MC-4

Figure 4-28 illustrates the turbidity distributions for small MCs with different MC concentrations. It is apparent that the high concentration yields lower turbidity than the low concentration for the four coagulant aids. Figure 4-29 shows the turbidity distributions for large MCs with different MC concentrations. The trend is similar with the small MC except for coagulant aid POL-EZ7736 (anionic). Comparing the above two figures, one can

see that the influence of MC concentration is more pronounced in the smaller diameter range.

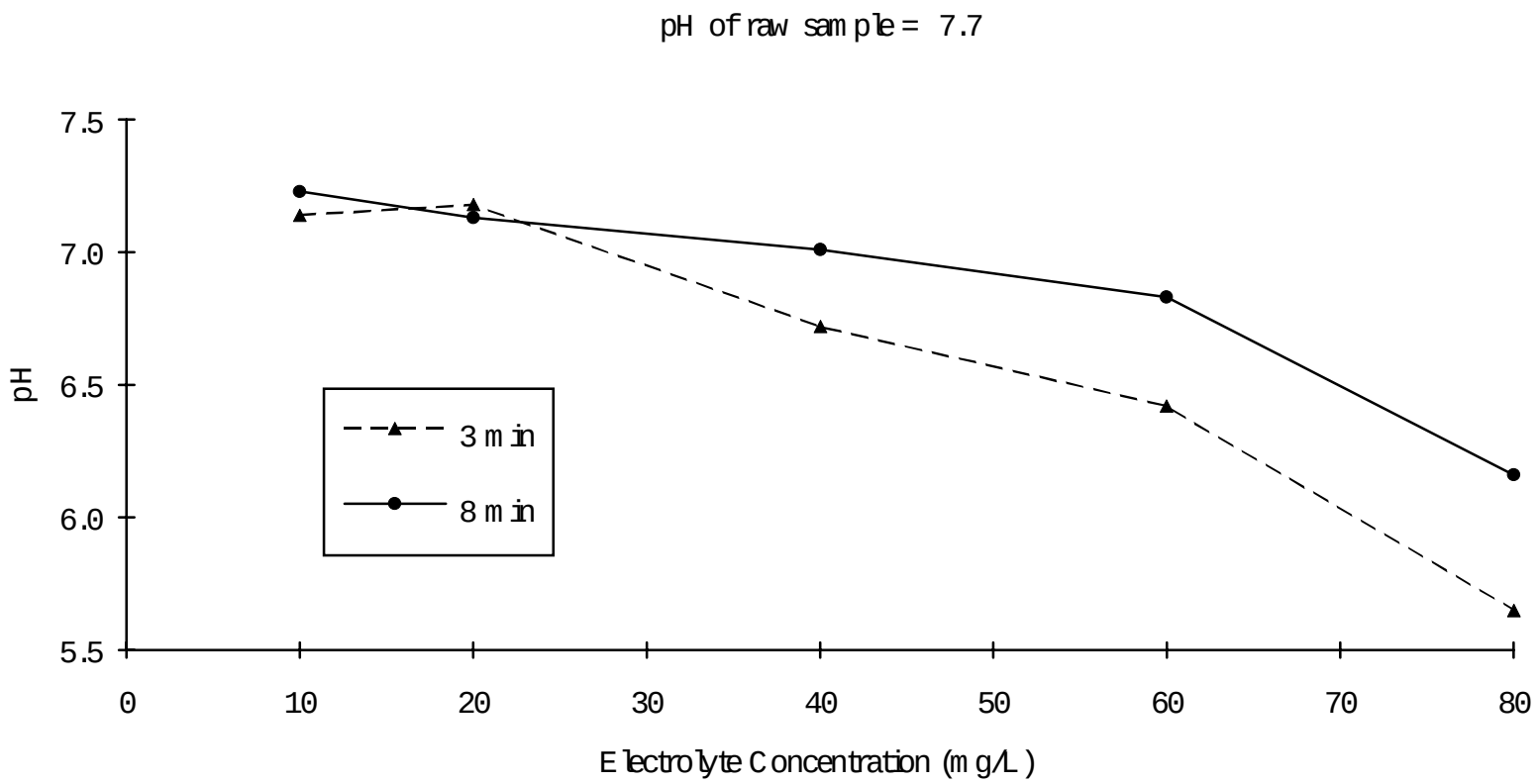
MC-1 versus MC-2 and MC-3 versus MC-4

Figure 4-30 compares the results of different MC sizes for low MC concentrations. Except for coagulant aid POL-EZ-2696 (non-ionic), large MCs yield lower turbidity. Figure 4-31 compares the results of different MC sizes for high MC concentrations. Unlike the situation for low MC concentration, the lower turbidity results were obtained from small MCs for all four coagulant aids. Figure 4-32 is a turbidity summary based on coagulant aid grouping.

Based on the turbidity analyses illustrated in Figure 4-33, MC-3, namely, 53——150 μm size range and 10 g/L dosage, yields the best results.

Turbidity versus Particle Count Rate

Figure 4-34 presents the correlation between particle count rate and turbidity. The correlation coefficient of turbidity and particle count rate was 0.5.

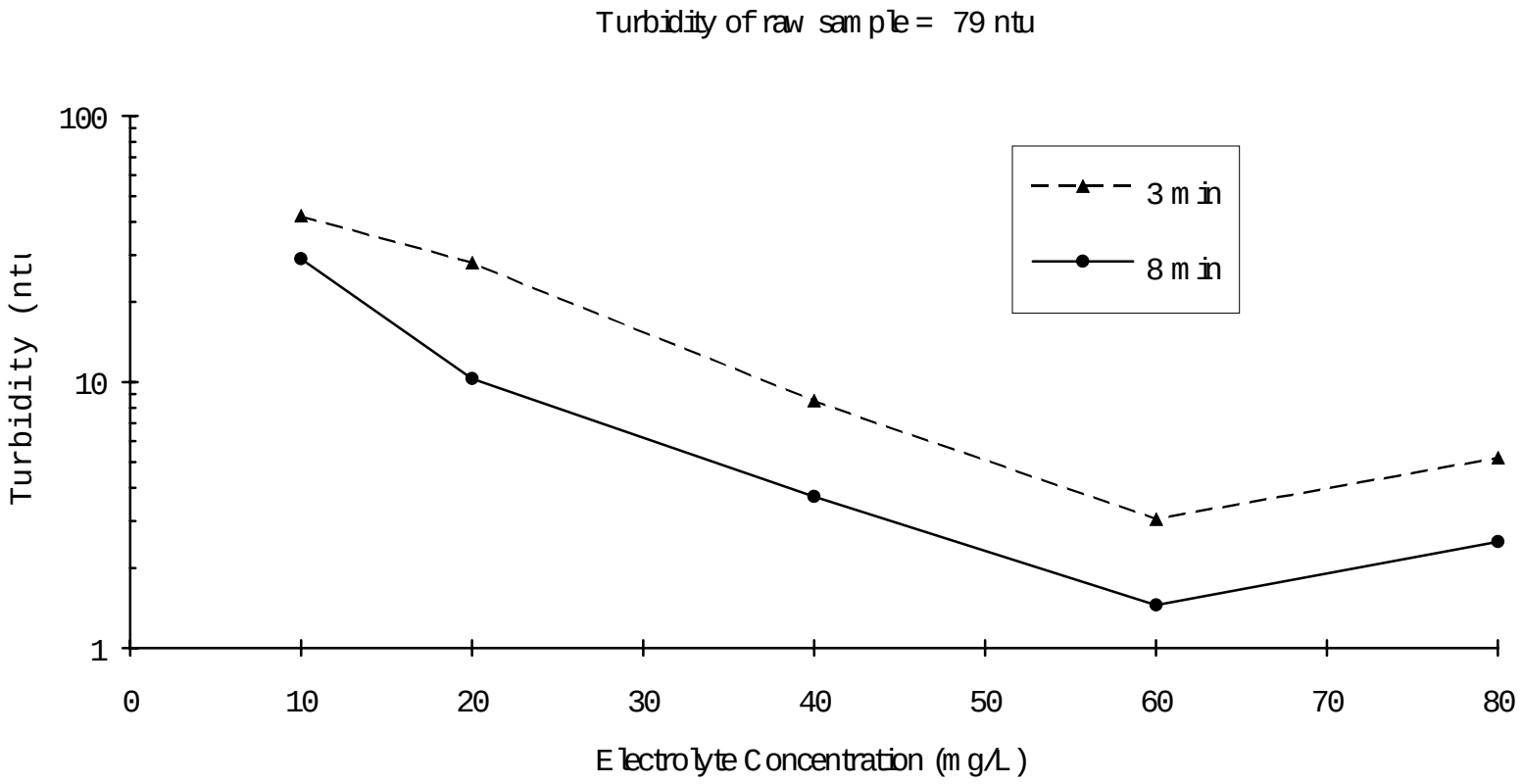


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

Settling Time: 3 and 8 minutes; Without Polyelectrolyte

Figure 4-4. Typical pH Distributions (Level-1)

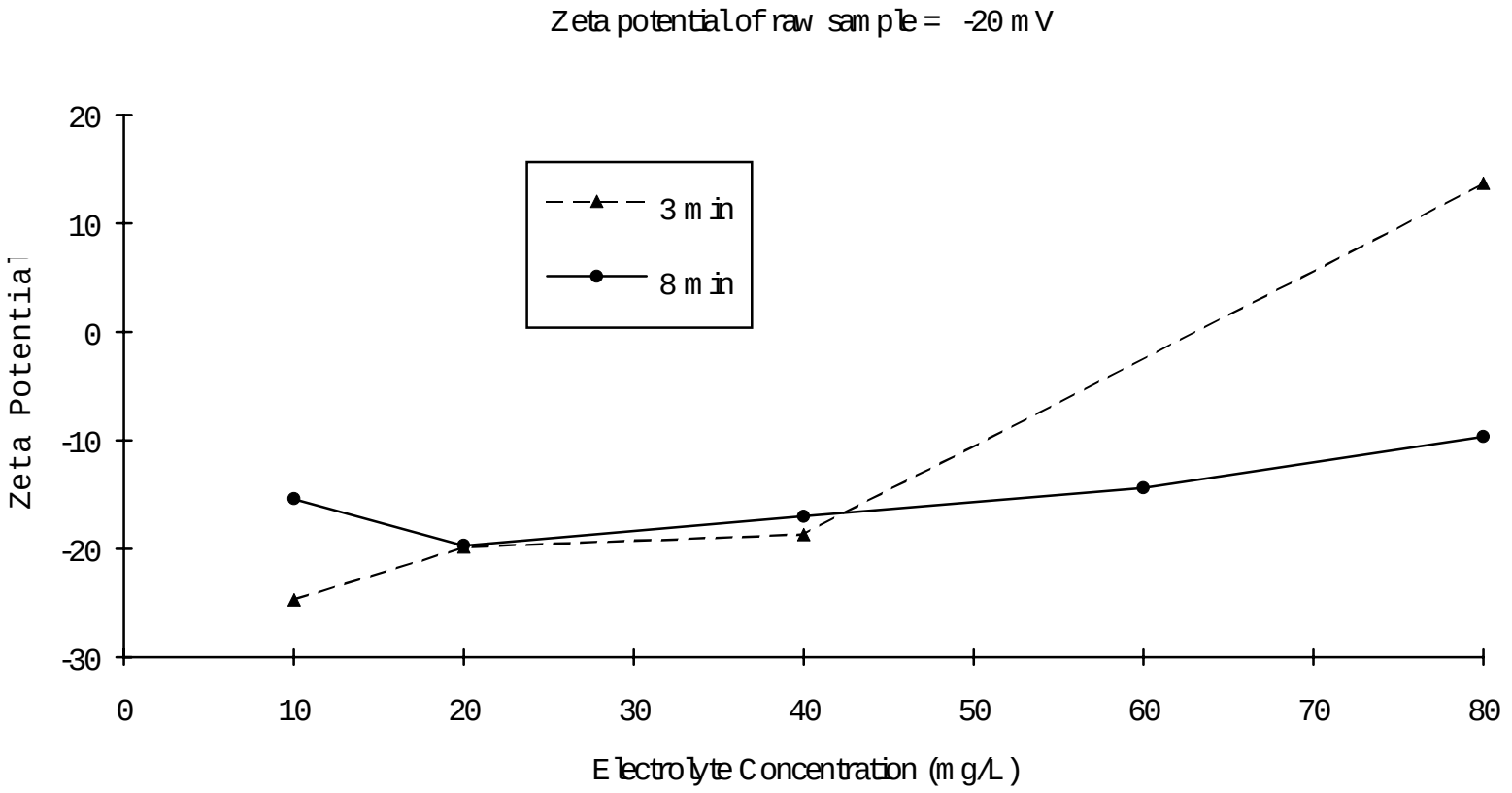


MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

Settling Time: 3 and 8 minutes; Without Polyelectrolyte

Figure 4-5. Turbidity Versus Coagulant Concentration (Level-1)

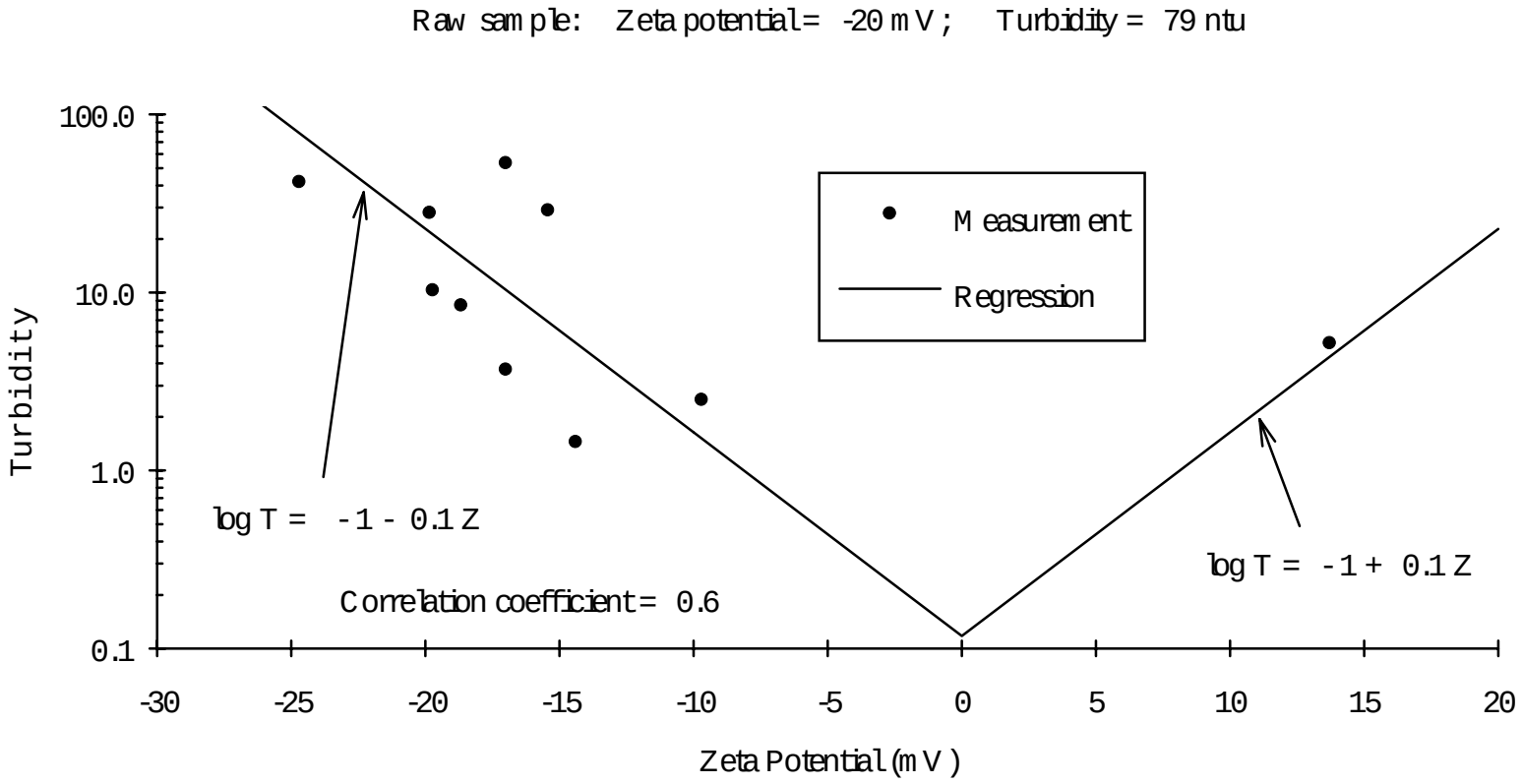


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

Without Polyelectrolyte

Figure 4-6. Zeta Potential Distributions (Level-1)

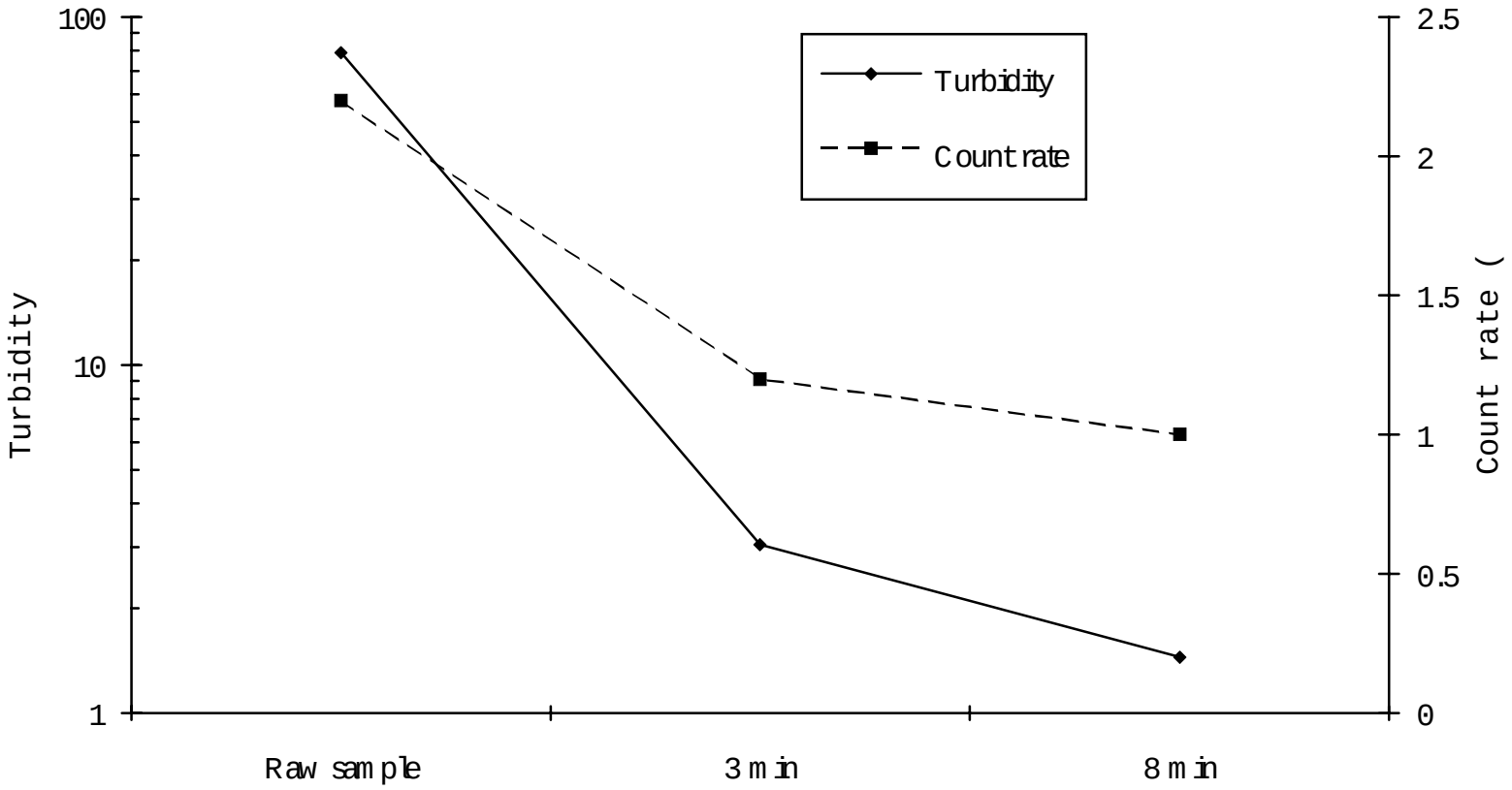


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

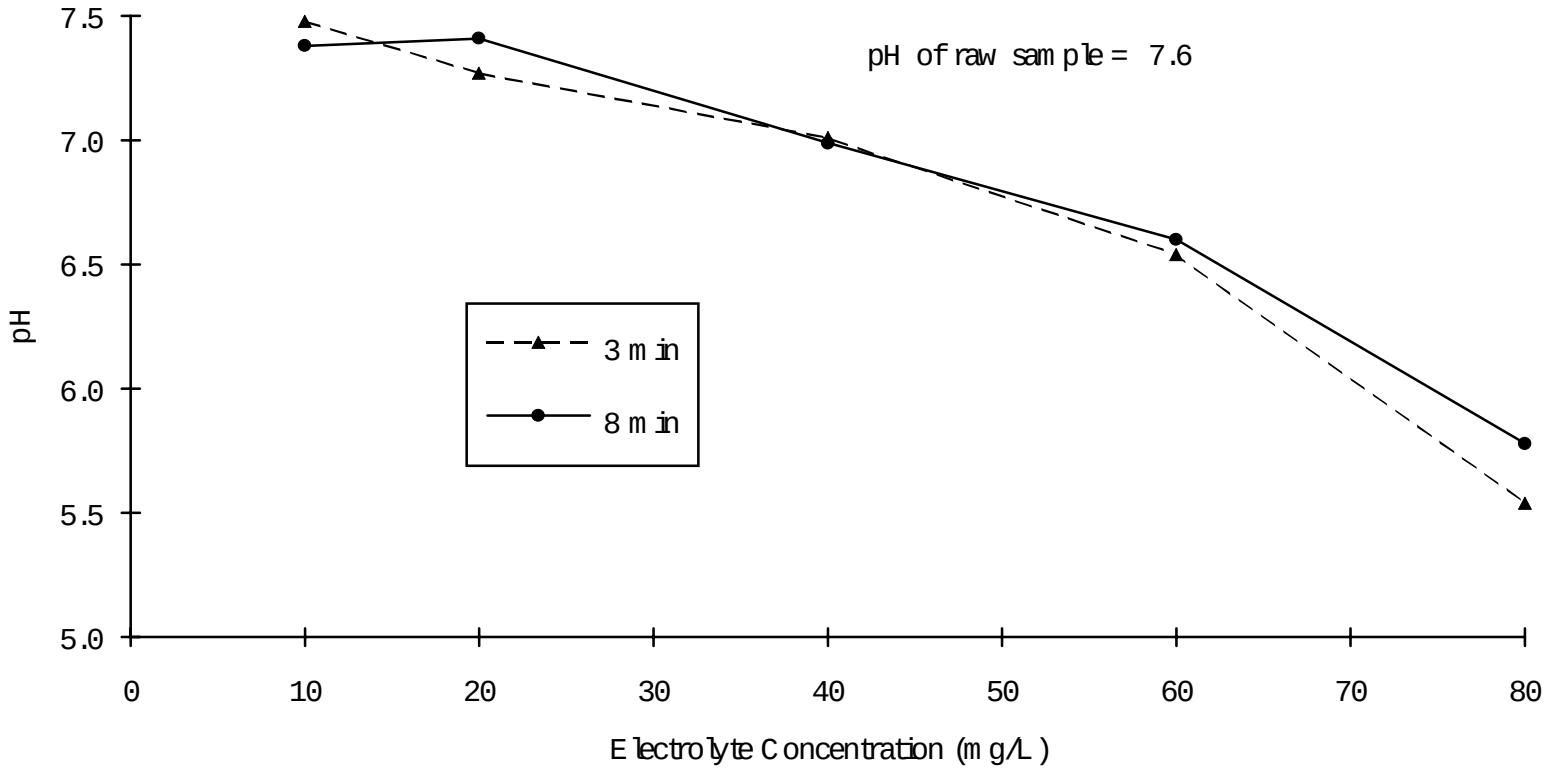
Without Polyelectrolyte

Figure 4-7. Correlation of Zeta Potential and Turbidity (Level-1)



MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 60 mg/L
Settling Time: 3 and 8 minutes; Without Polyelectrolyte

Figure 4-8. Particle Count Rate for the Best Coagulant Concentration (Level-1)



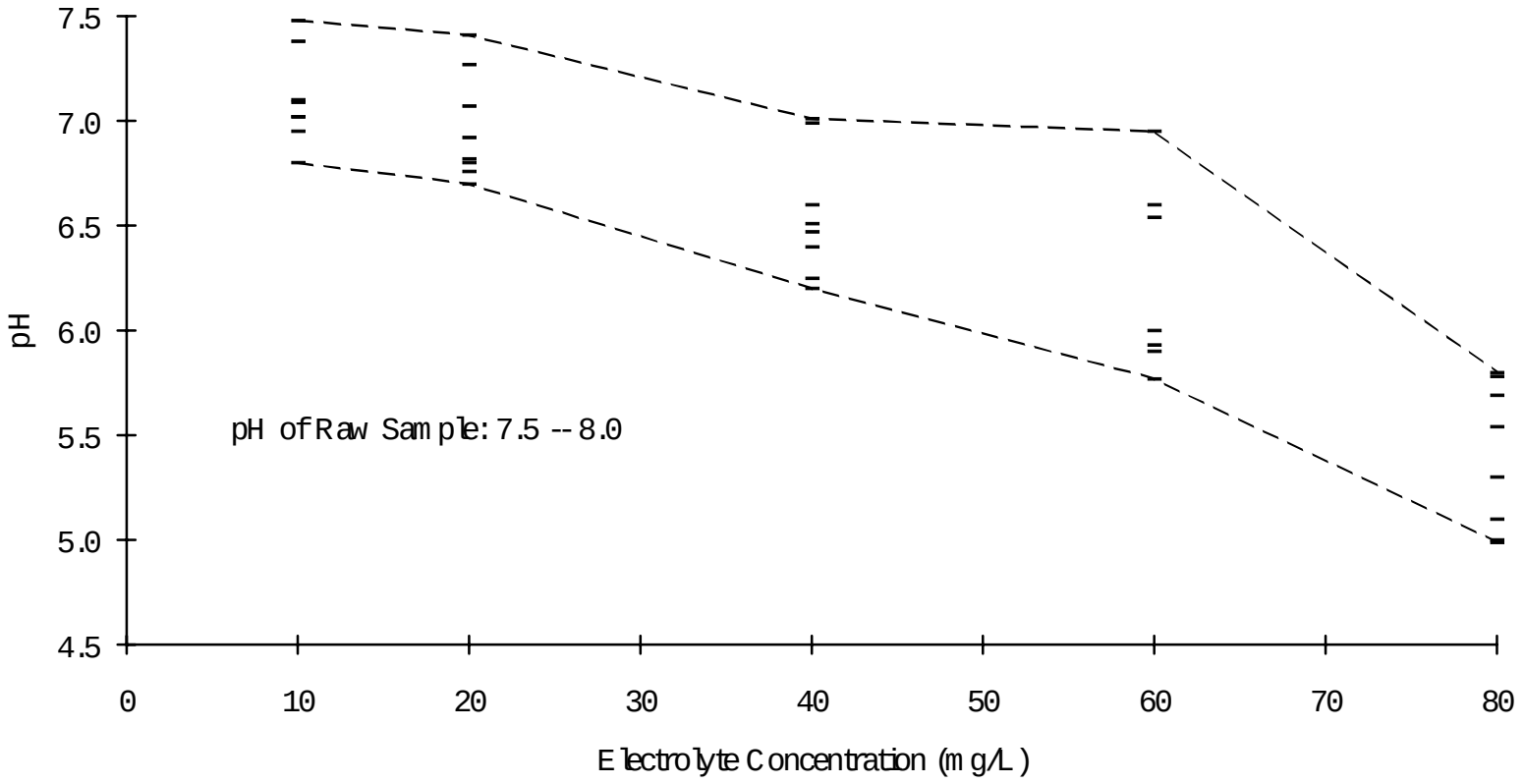
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-3: Polyelectrolyte POL-EZ-2696 Concentration = 1 mg/L

Settling Time: 3 and 8 minutes

Figure 4-9. Typical pH Distributions (Level-2)



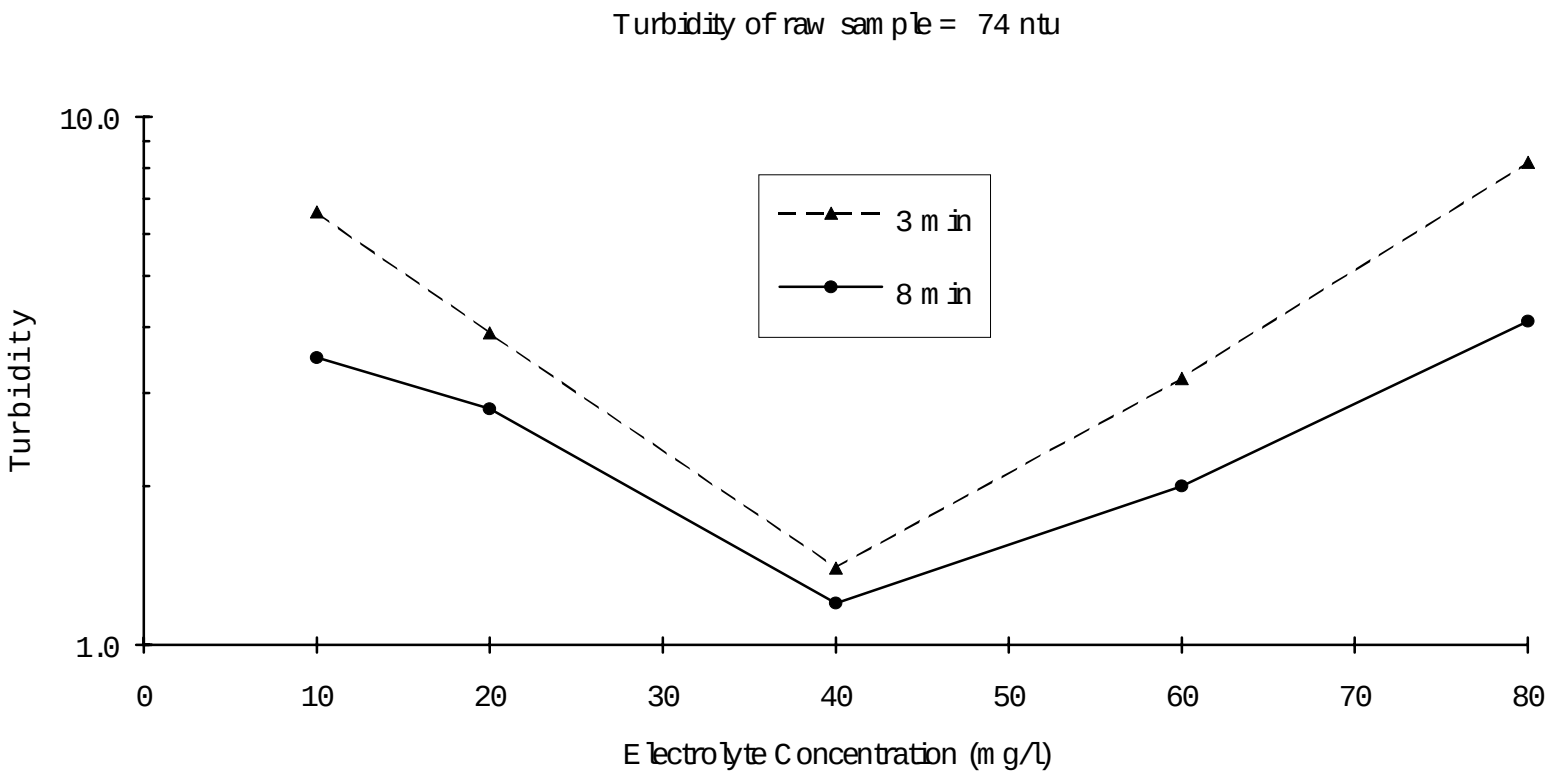
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-1: POL-EZ-2466; PE-2: POL-EZ-3466; PE-3: POL-EZ-2696; PE-4: POL-EZ-7736

Polyelectrolyte Concentration = 1 mg/L; Settling Time: 3 and 8 minutes

Figure 4-10. Summary of pH Distributions (Level-2)



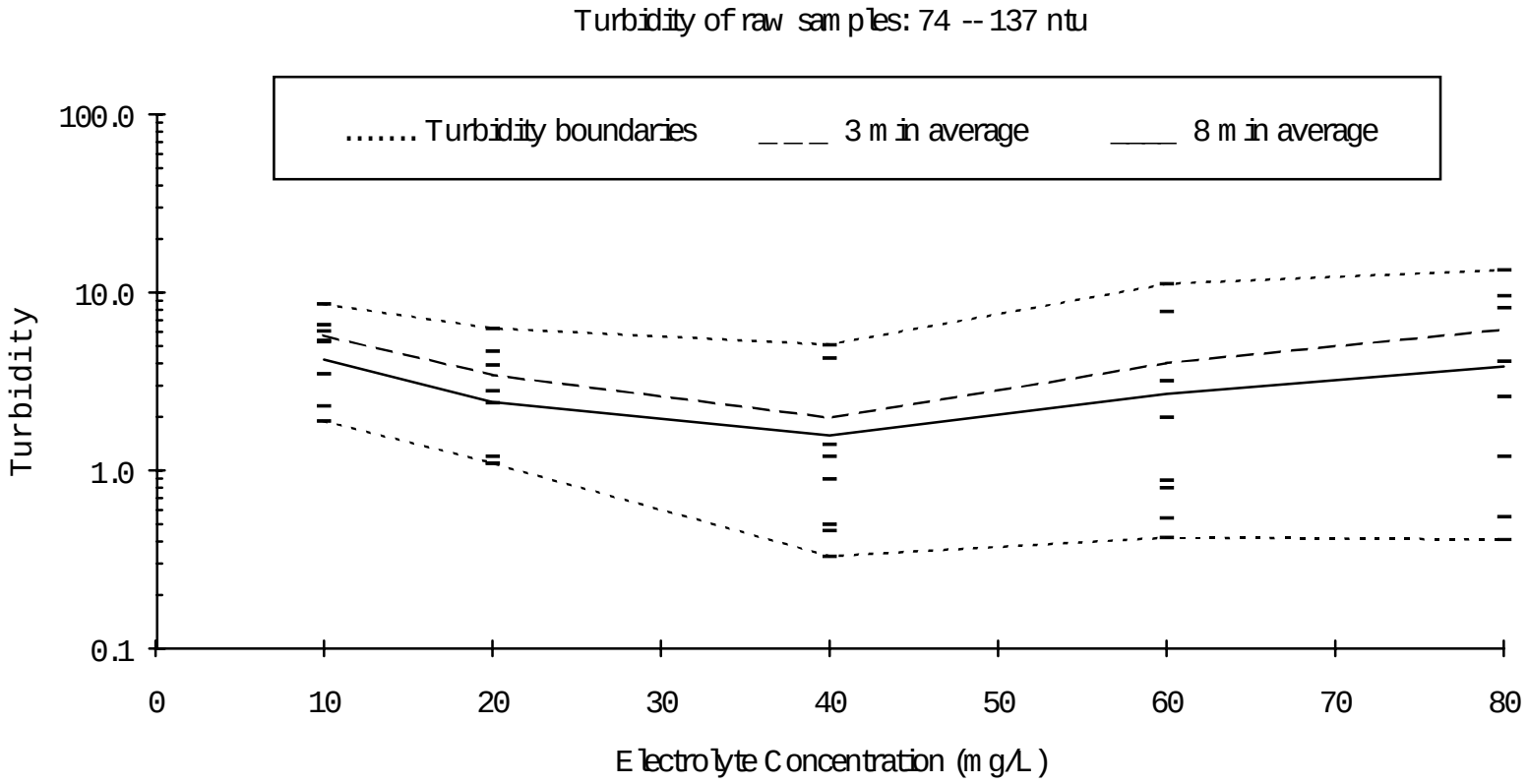
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-4: Polyelectrolyte POL-EZ-7736 Concentration = 1 mg/L

Settling Time: 3 and 8 minutes

Figure 4-11. Typical Turbidity Distributions (Level-2)



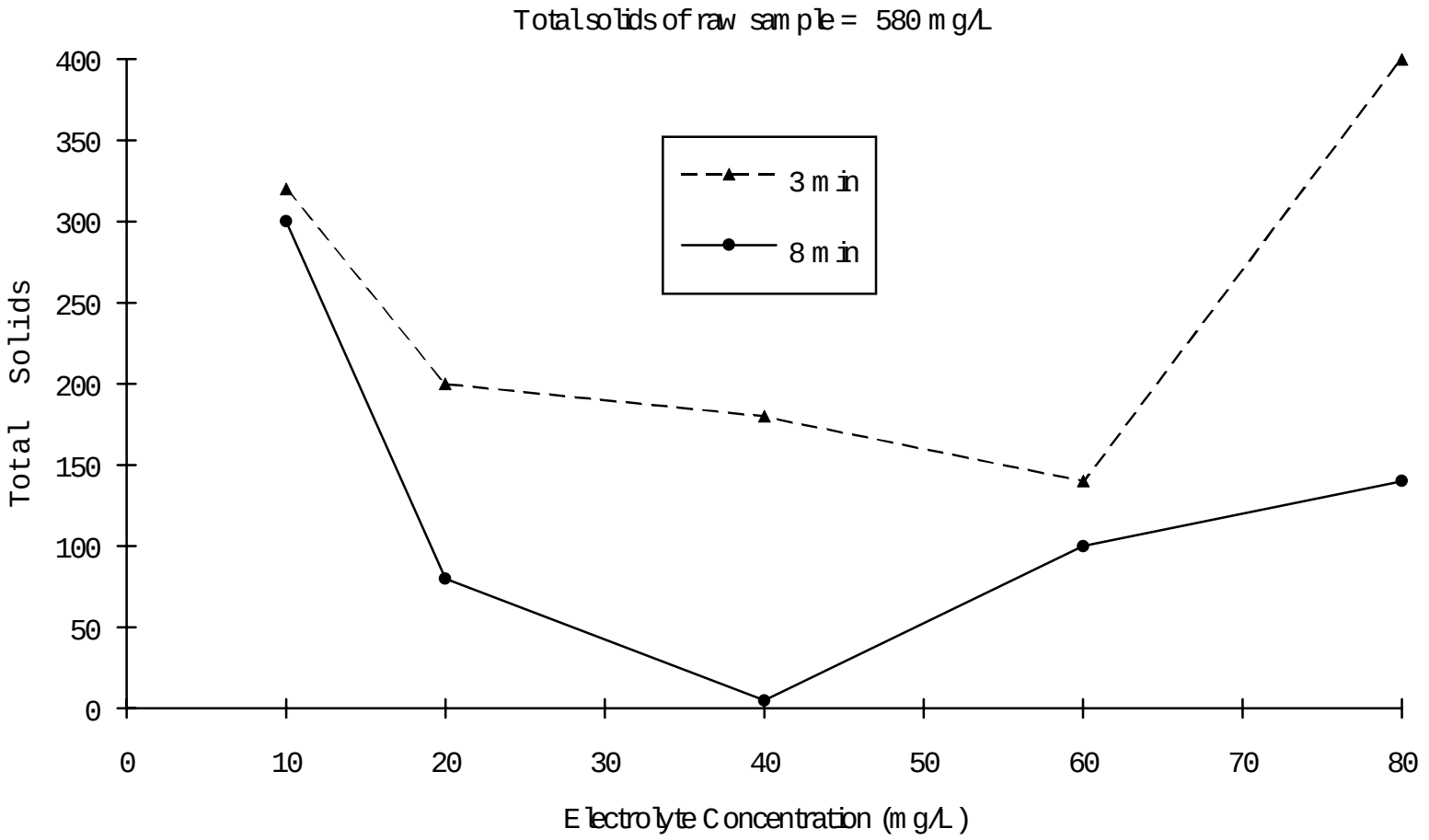
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-1: POL-EZ-2466; PE-2: POL-EZ-3466; PE-3: POL-EZ-2696; PE-4: POL-EZ-7736

Polyelectrolyte Concentration = 1 mg/L; Settling Time: 3 and 8

Figure 4-12. Summary of Turbidity Distributions (Level-2)

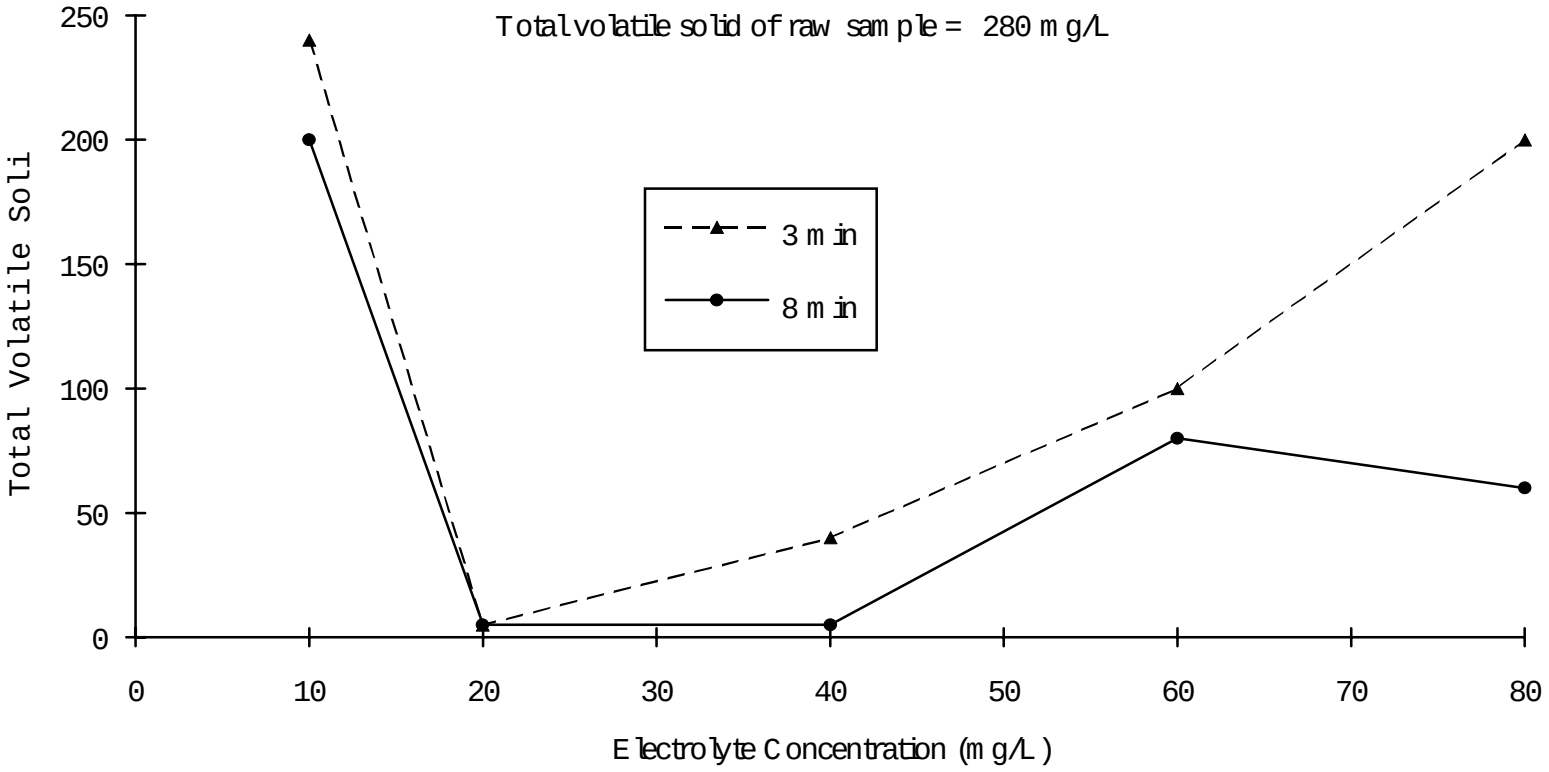


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-3: Polyelectrolyte POL-EZ-2696 Concentration = 1

Figure 4-13. Total Solids Distributions (Level-2)



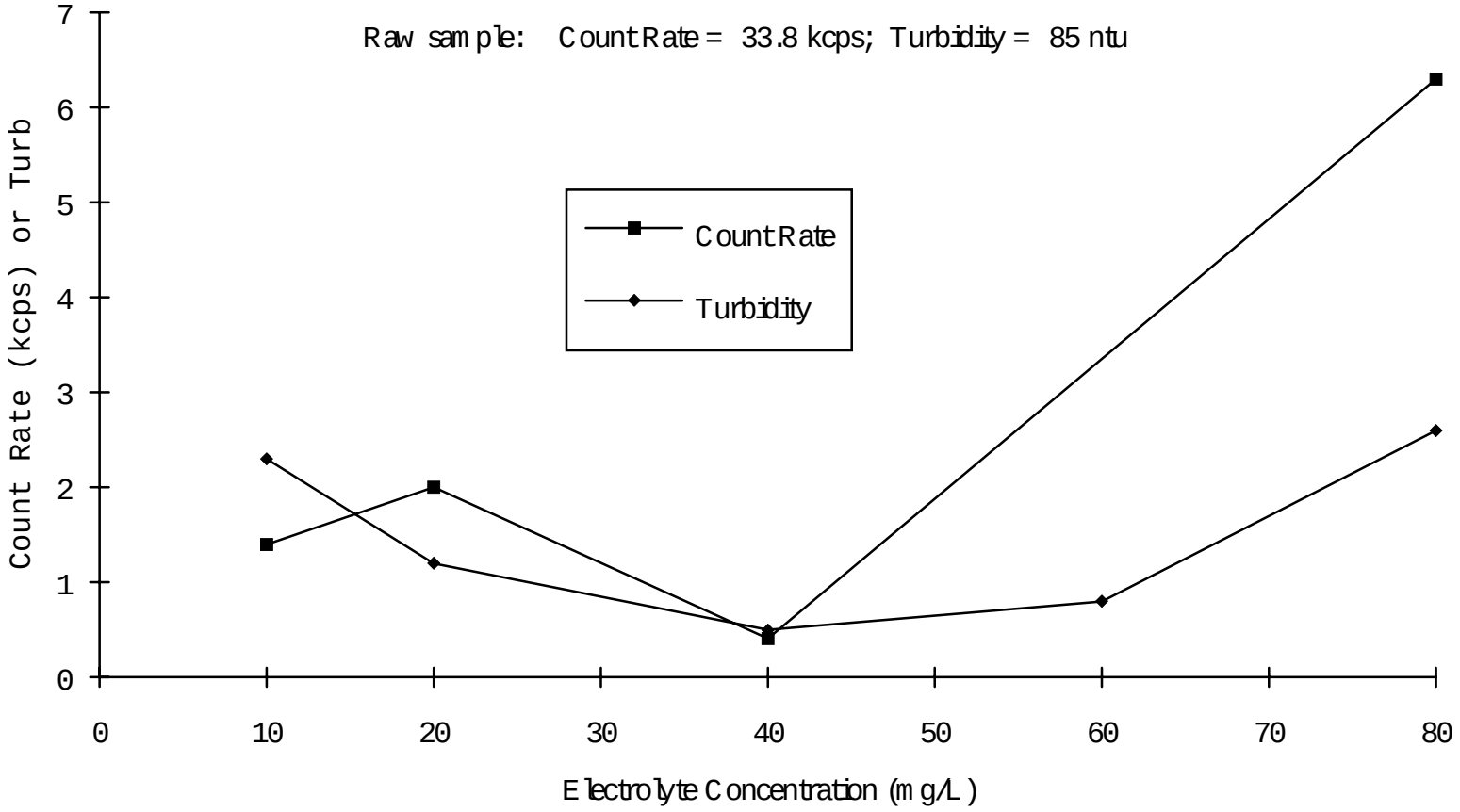
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-3: Polyelectrolyte POL-EZ-2696 Concentration = 1 mg/L

Settling Time: 3 and 8 minutes

Figure 4-14. Total Volatile Solids Distributions (Level-2)

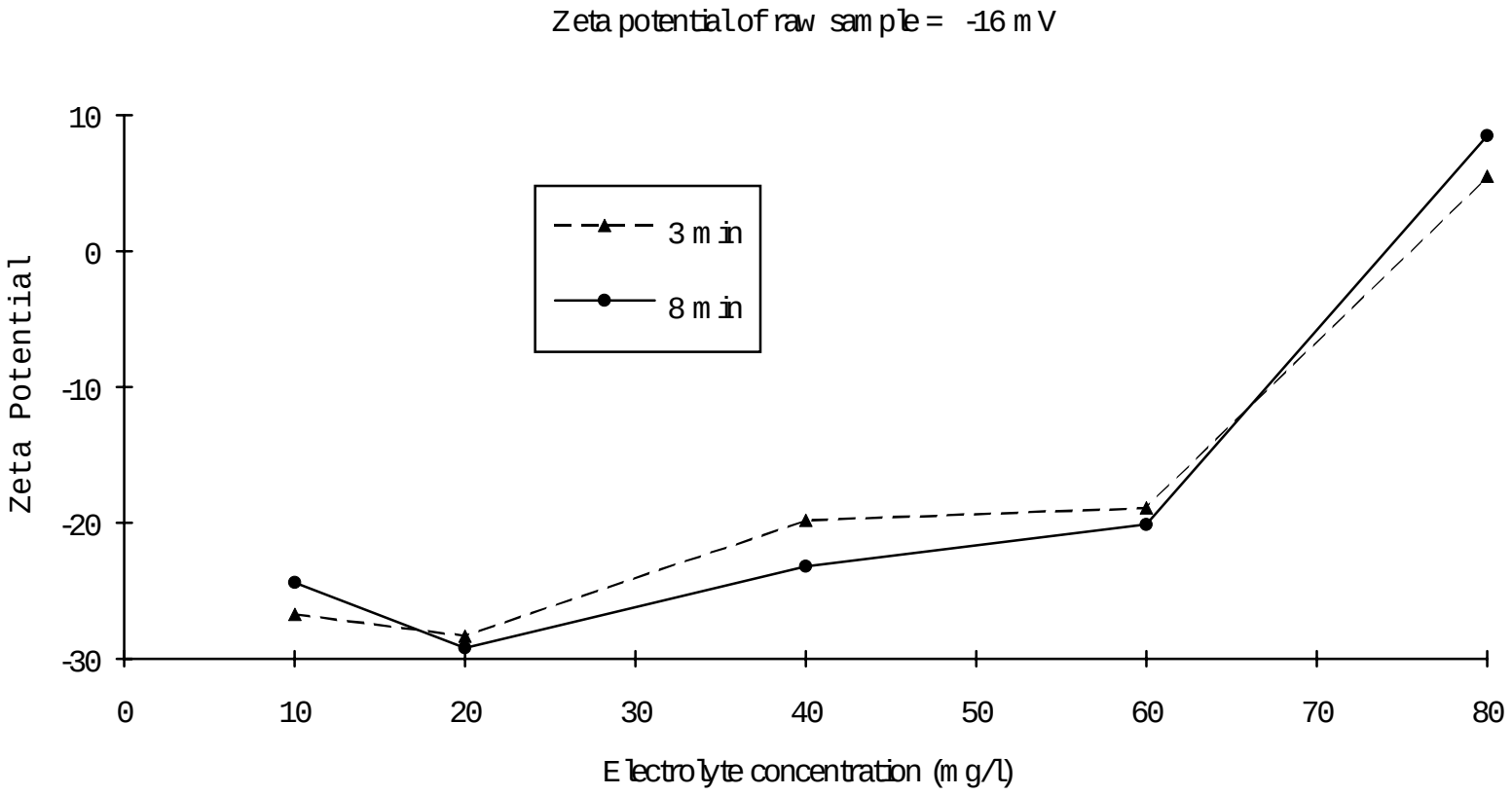


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-3: Polyelectrolyte POL-EZ-2696 Concentration = 1

Figure 4-15. A Comparison of Turbidity and Particle Count Rate (Level-2)



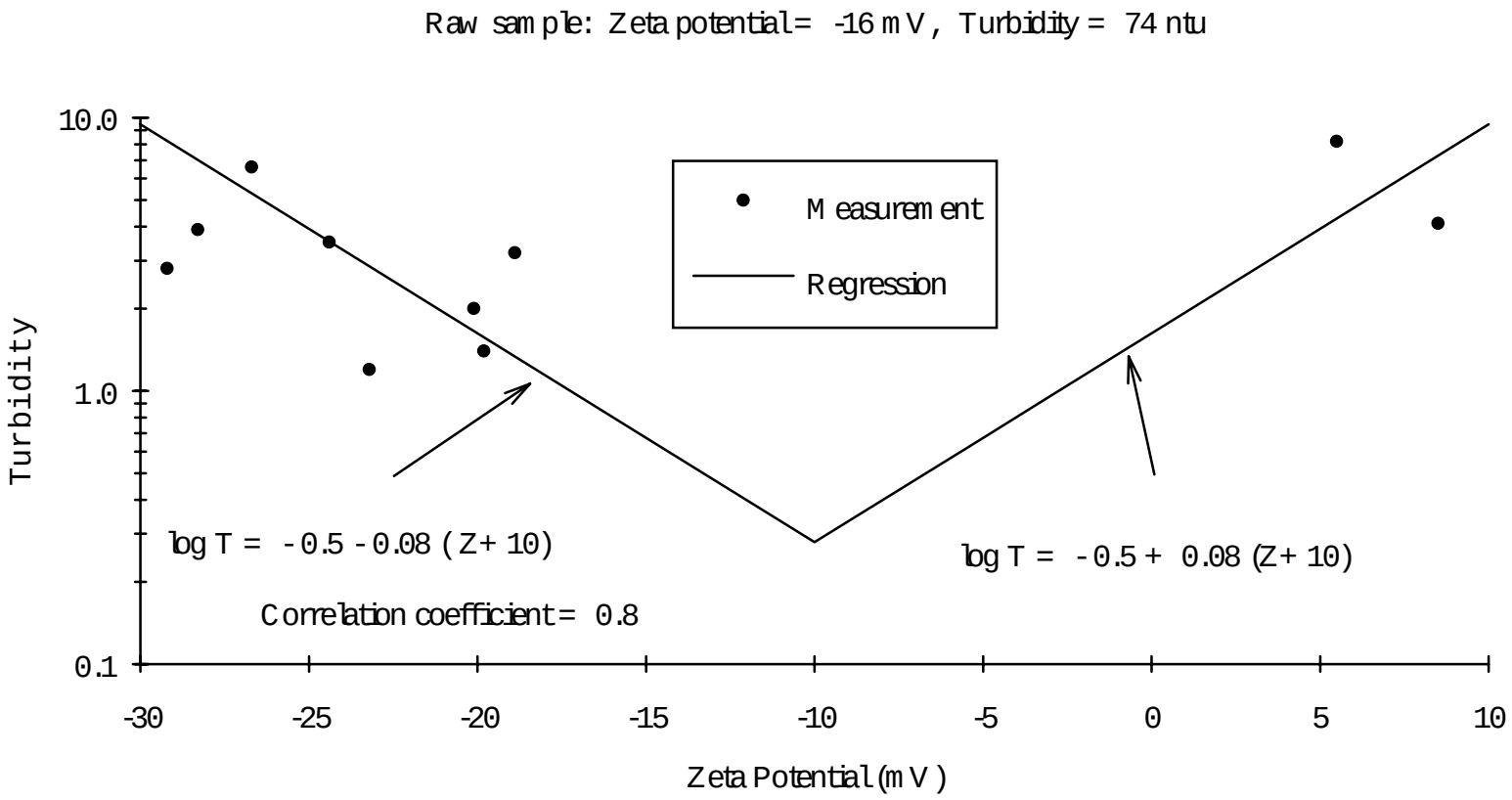
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

PE-4: Polyelectrolyte POL-EZ-7736 Concentration = 1 mg/L

Settling Time: 3 and 8 minutes

Figure 4-16. Zeta Potential Distributions (Level-2)

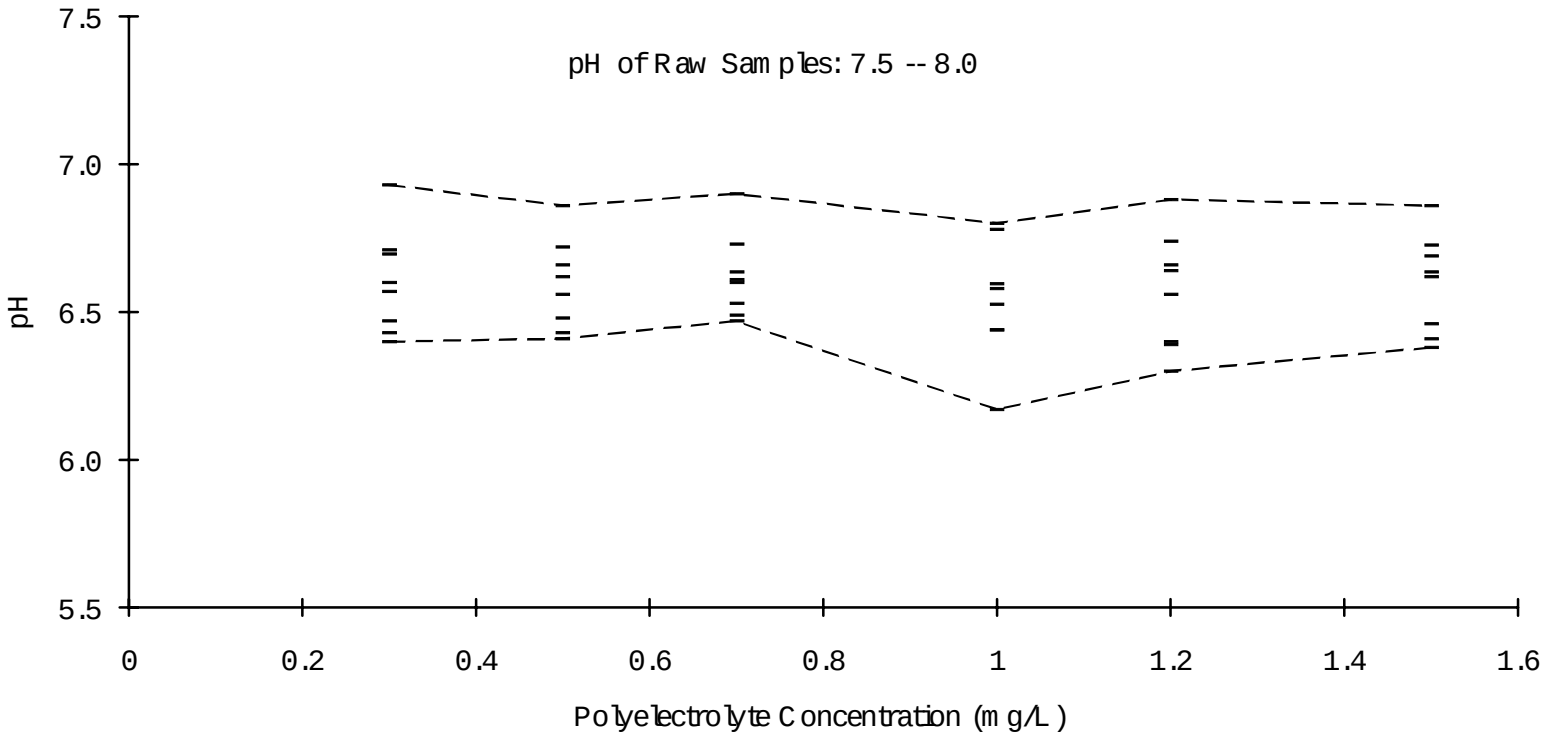


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 10—80 mg/L

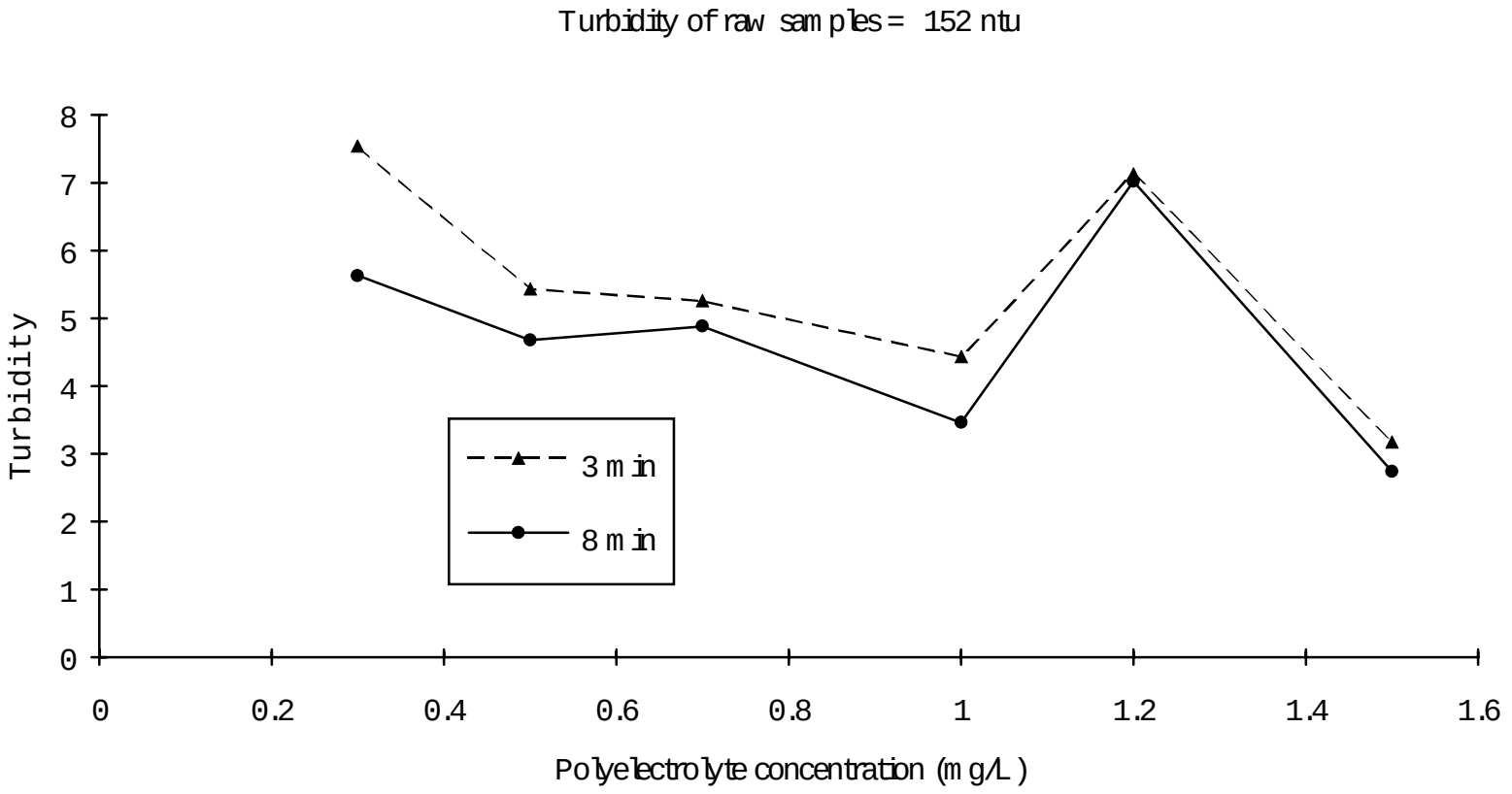
PE-4: Polyelectrolyte POL-EZ-7736 Concentration = 1

Figure 4-17. Correlation of Zeta Potential and Turbidity (Level-2)



MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Polyelectrolyte: PE-1: POL-EZ-2466; PE-2: POL-EZ-3466;
PE-3: POL-EZ-2696; PE-4: POL-EZ-7736
Polyelectrolyte Concentration = 0.3—1.5 mg/L
Settling Time: 3 and 8 minutes

Figure 4-18. Summary of pH Distributions (Level-3)



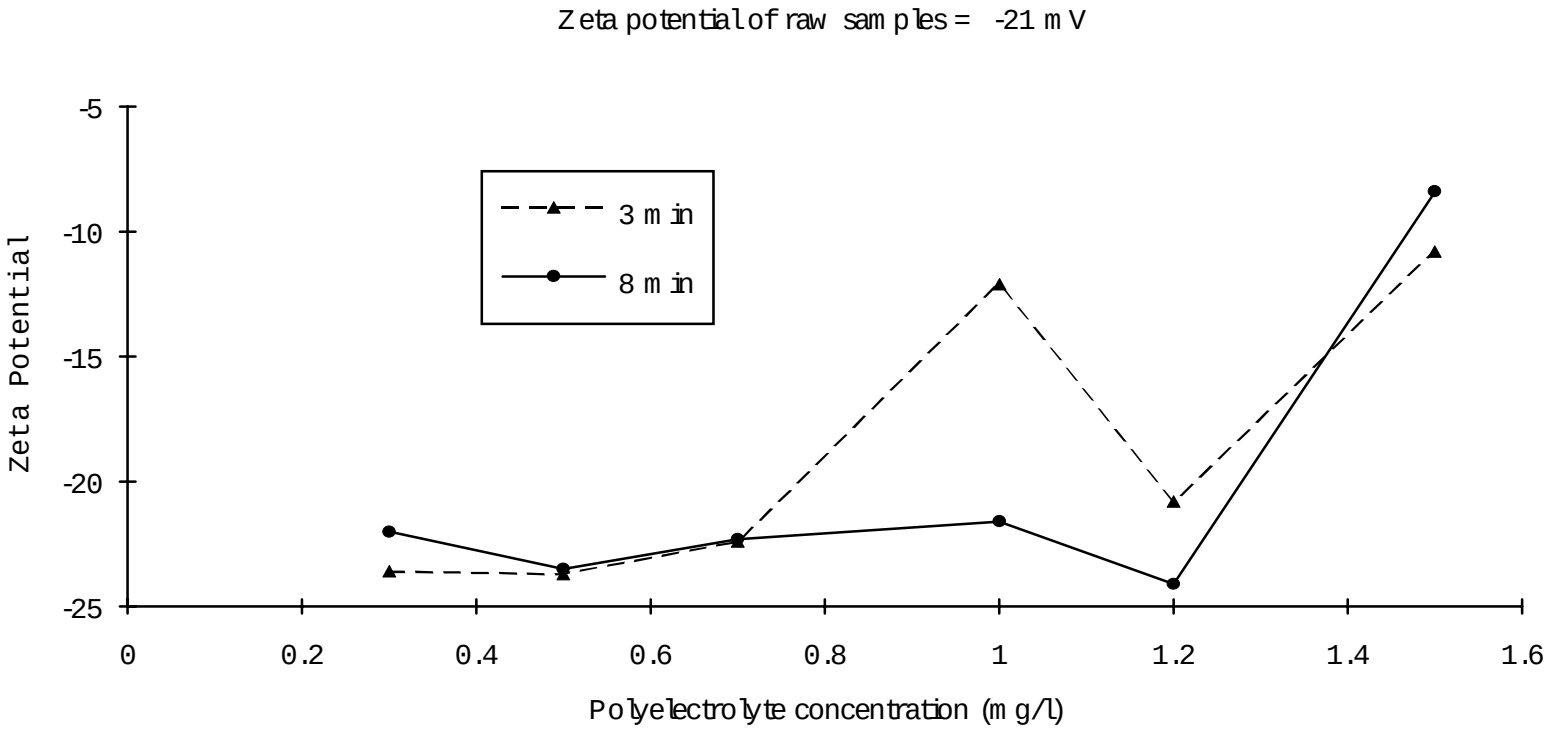
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-3: POL-EZ-2696; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-19. Turbidity Distributions (Level-3; POL-EZ-2696)



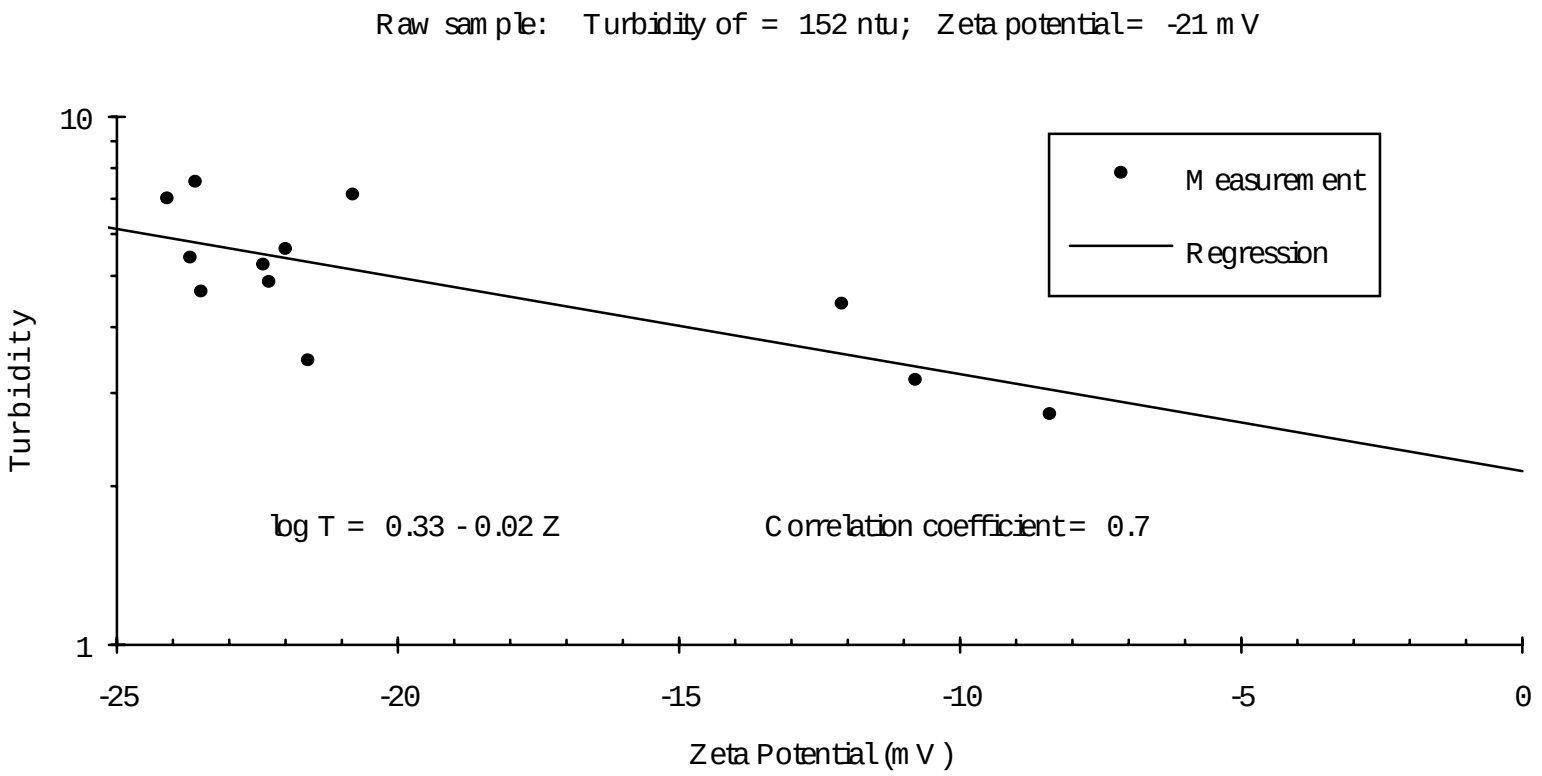
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-3: POL-EZ-2696; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-20. Zeta Potential Distributions (Level-3; POL-EZ-2696)



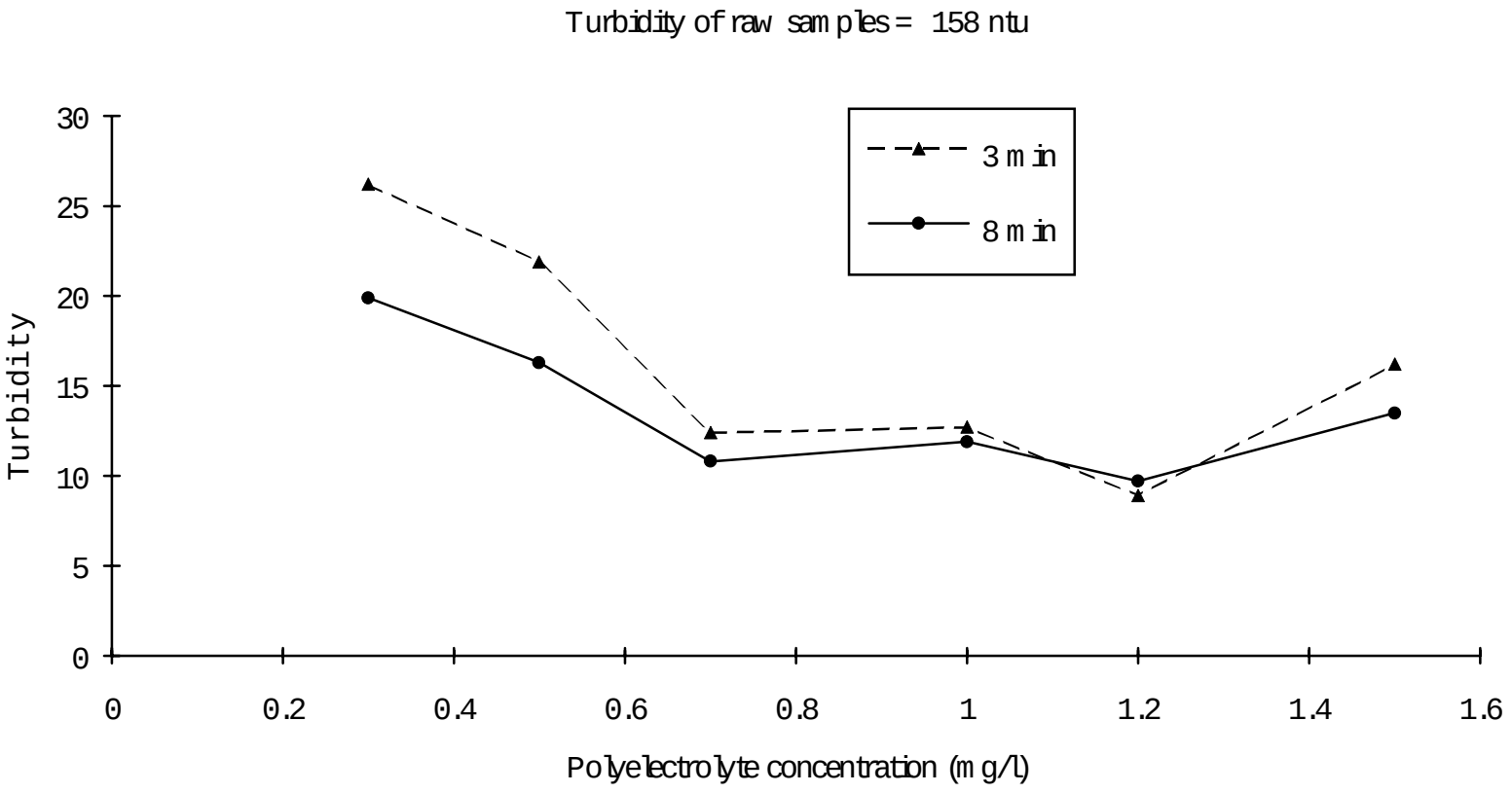
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-3: POL-EZ-2696; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-21. Correlation of Zeta Potential and Turbidity (Level-3)



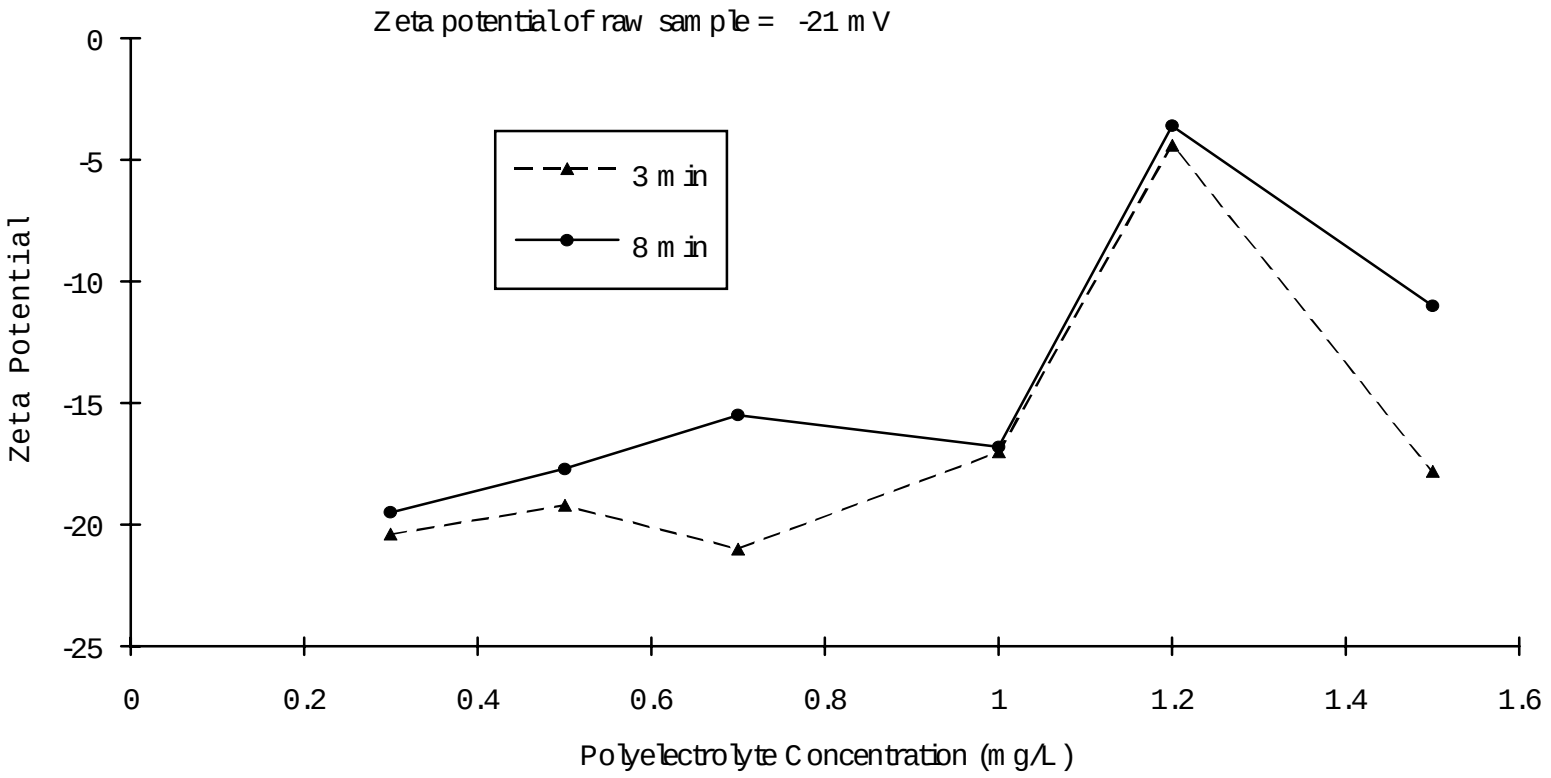
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-3: POL-EZ-2696; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-22. Turbidity Distributions (Level-3; POL-EZ-2466)



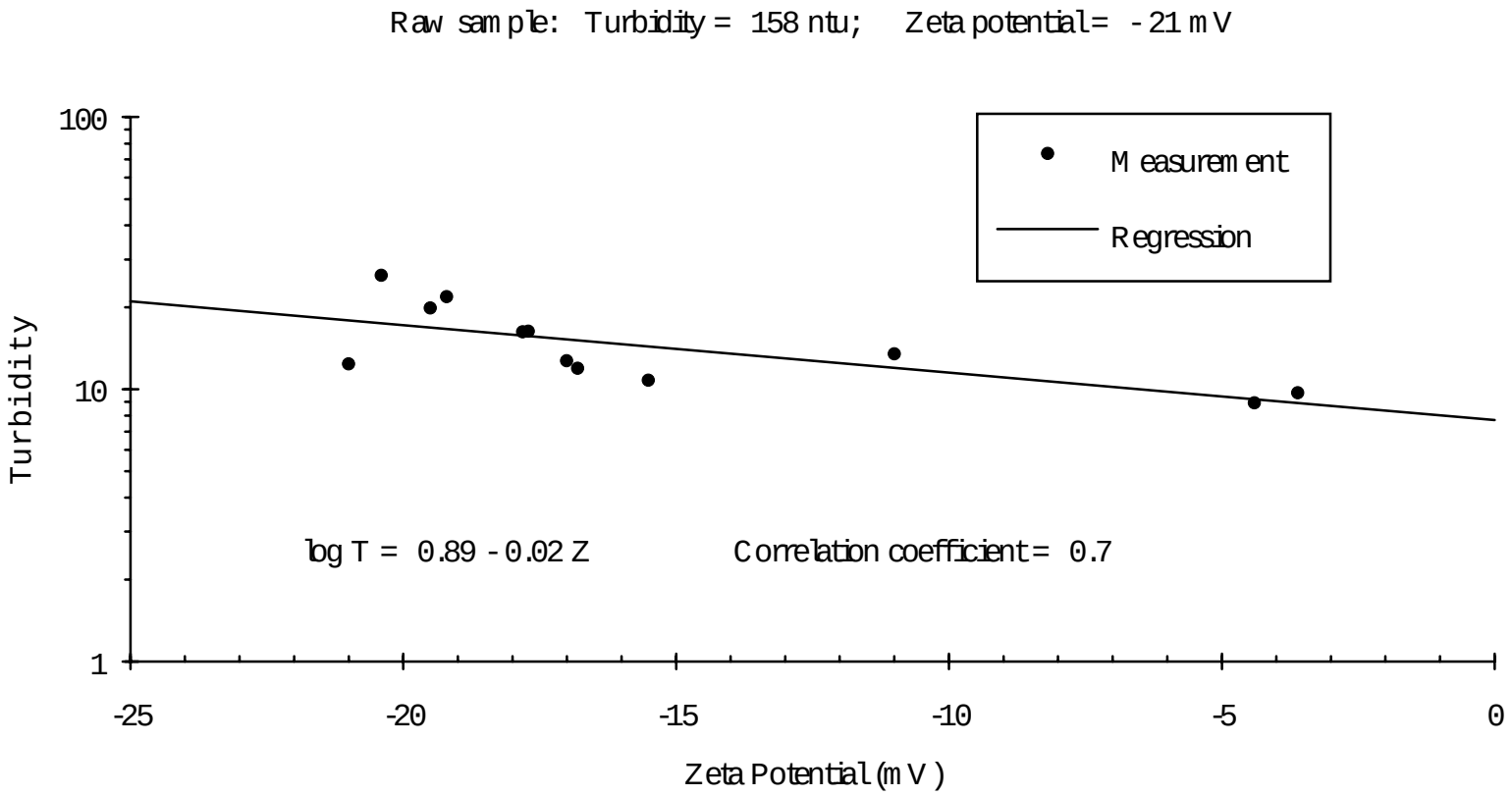
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-1: POL-EZ-2466; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-23. Zeta Potential Distributions (Level-3; POL-EZ-2466)

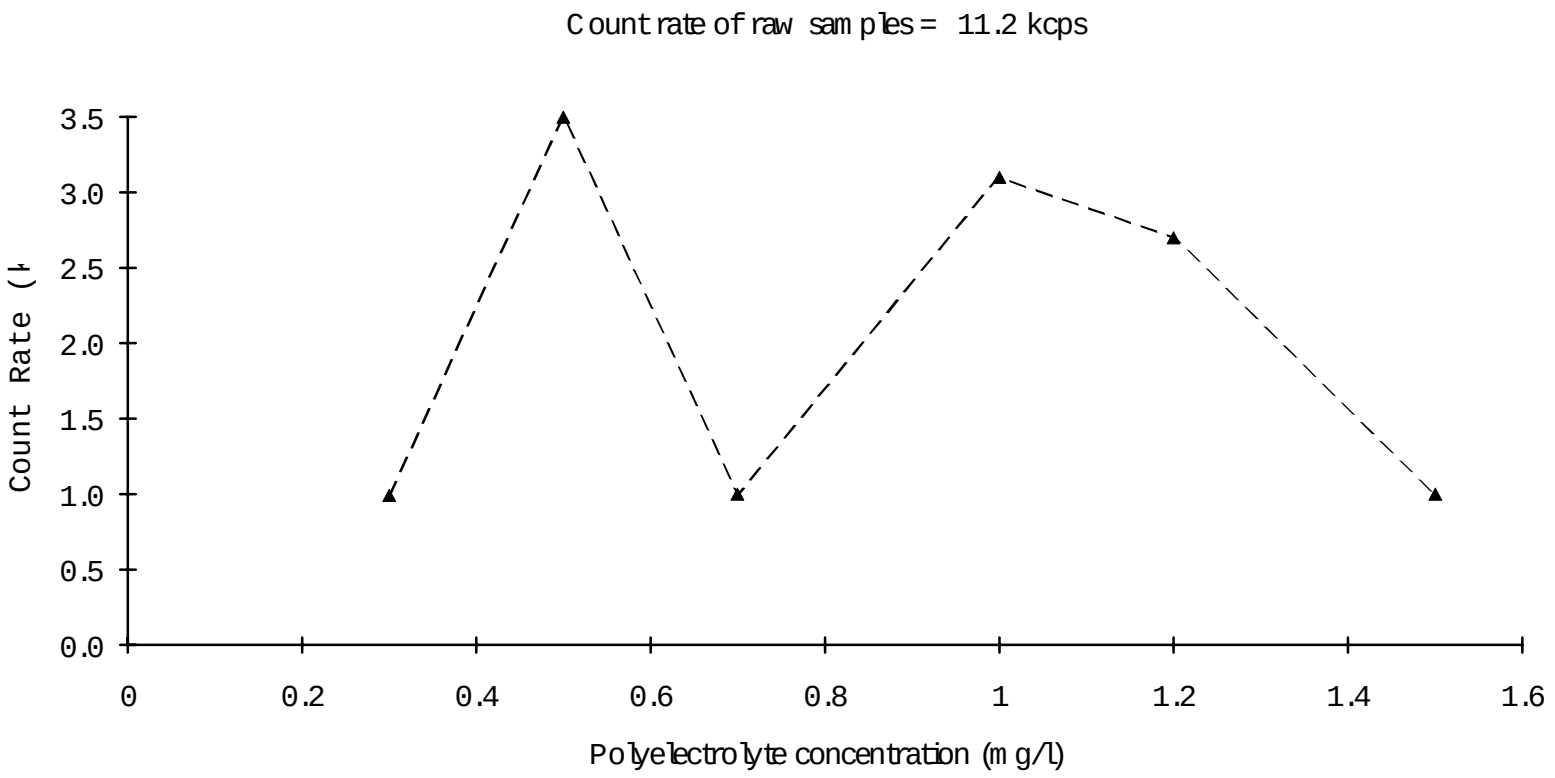


MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-1: POL-EZ-2466; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Figure 4-24. Correlation of Zeta Potential and Turbidity (Level-3)



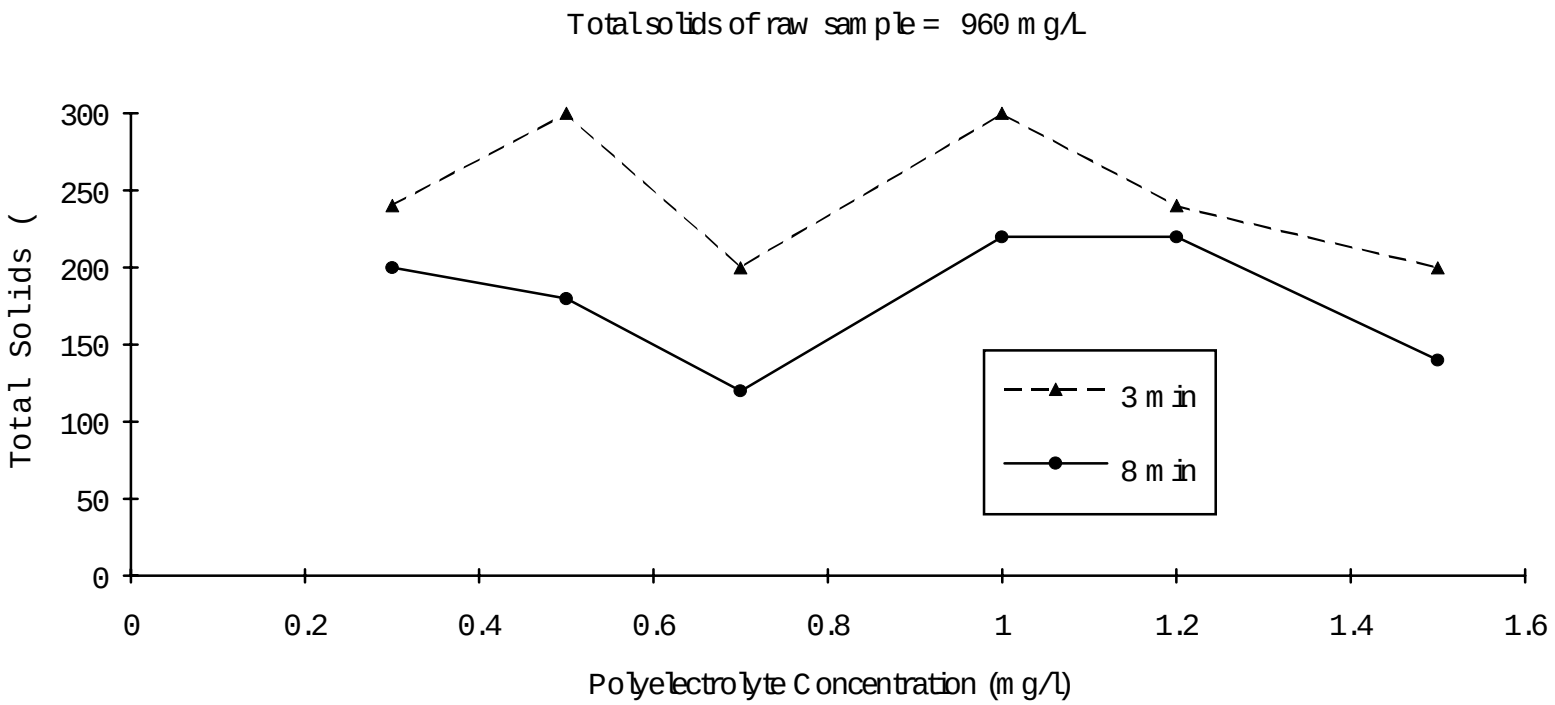
MC-1: MC Size Range = 53—150 μm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-1: POL-EZ-2466; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 minutes

Figure 4-25. Particle Count Rate Distribution (Level-3; POL-EZ-2466)



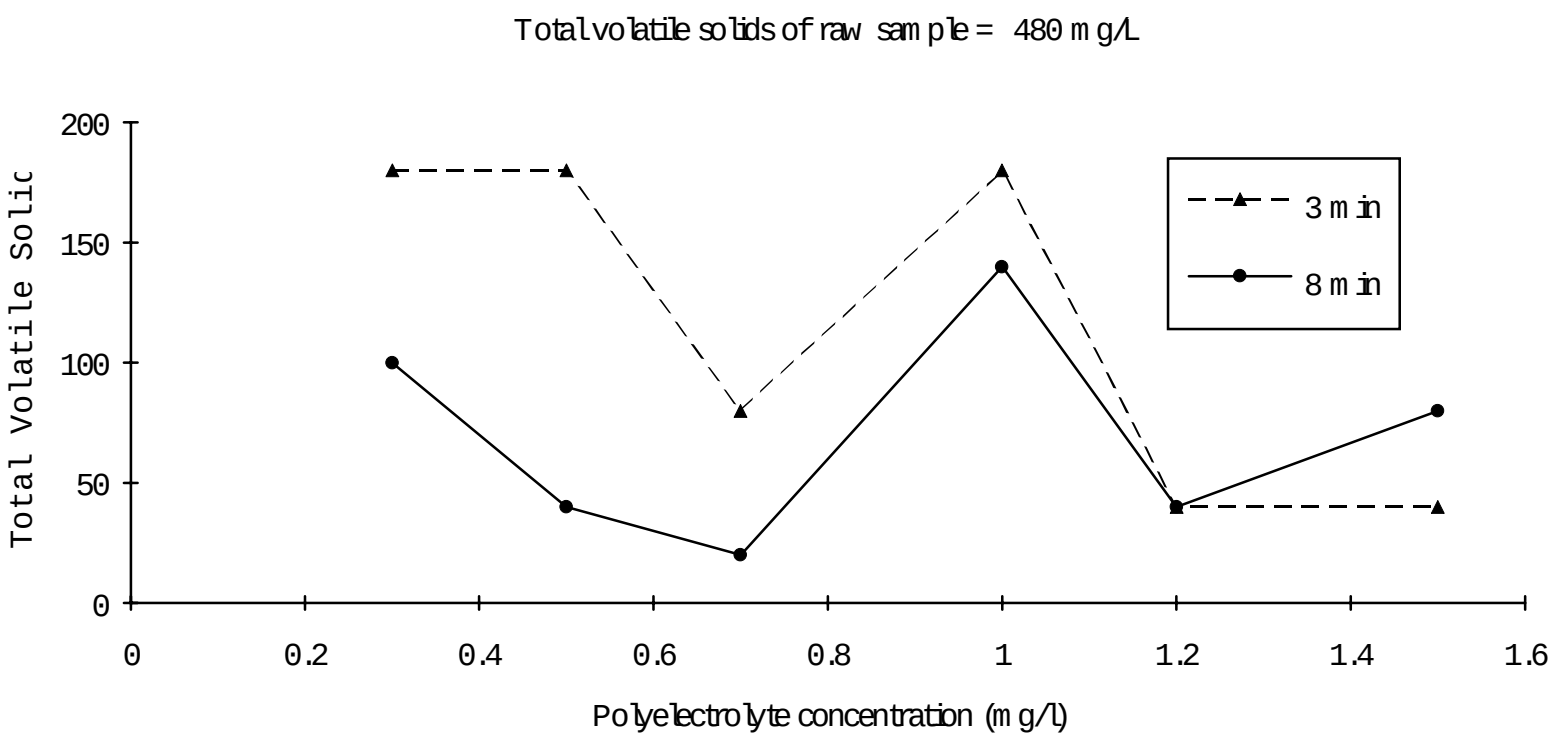
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-1: POL-EZ-2466; Polyelectrolyte Concentration = 0.3—1.5 mg/L

Settling Time: 3 and 8 minutes

Figure 4-26. Total Solids Distributions (Level-3; POL-EZ-2466)



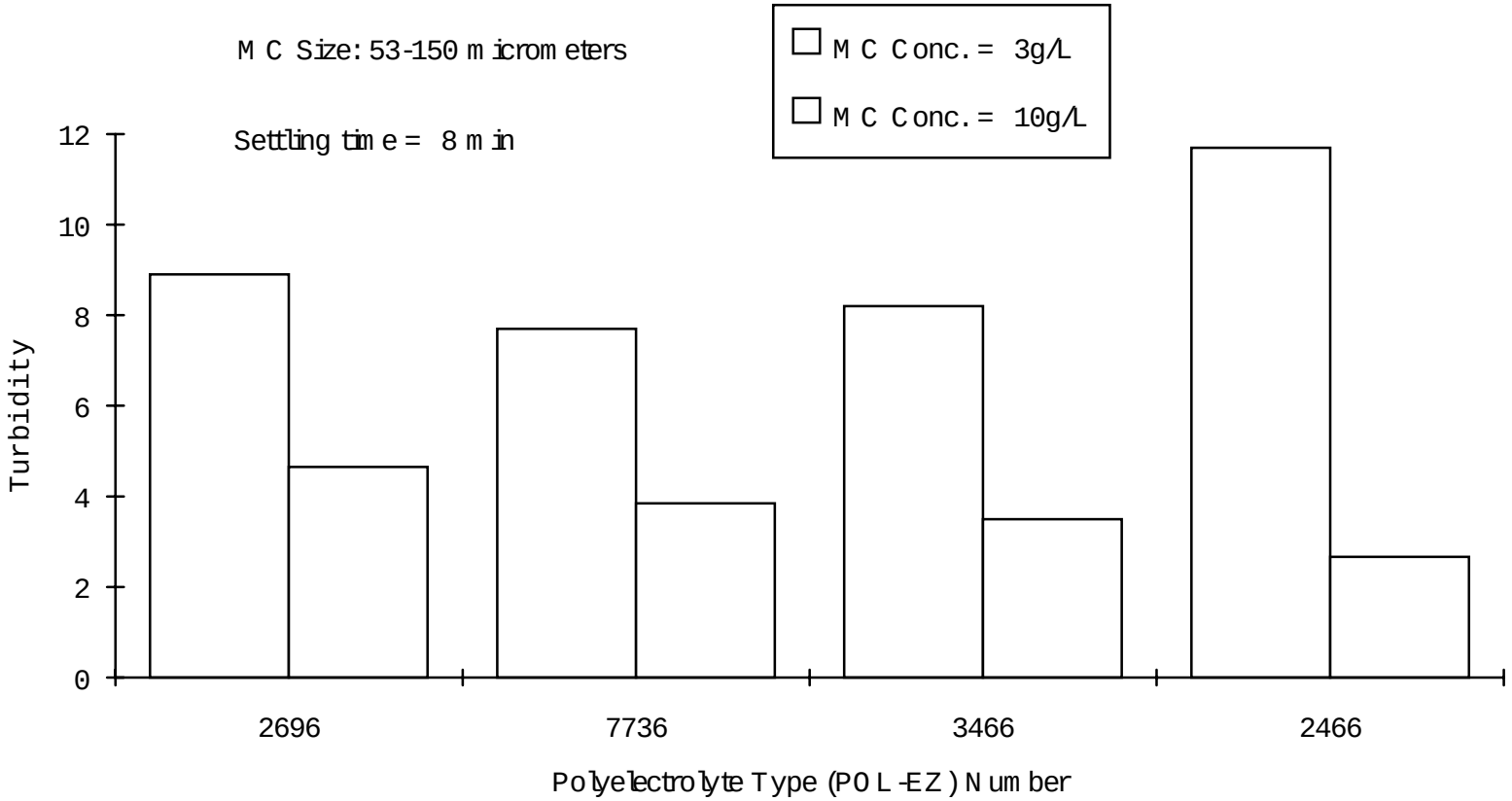
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 g/L

E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L

Polyelectrolyte: PE-1: POL-EZ-2466; Polyelectrolyte Concentration = 0.3—1.5 mg/L

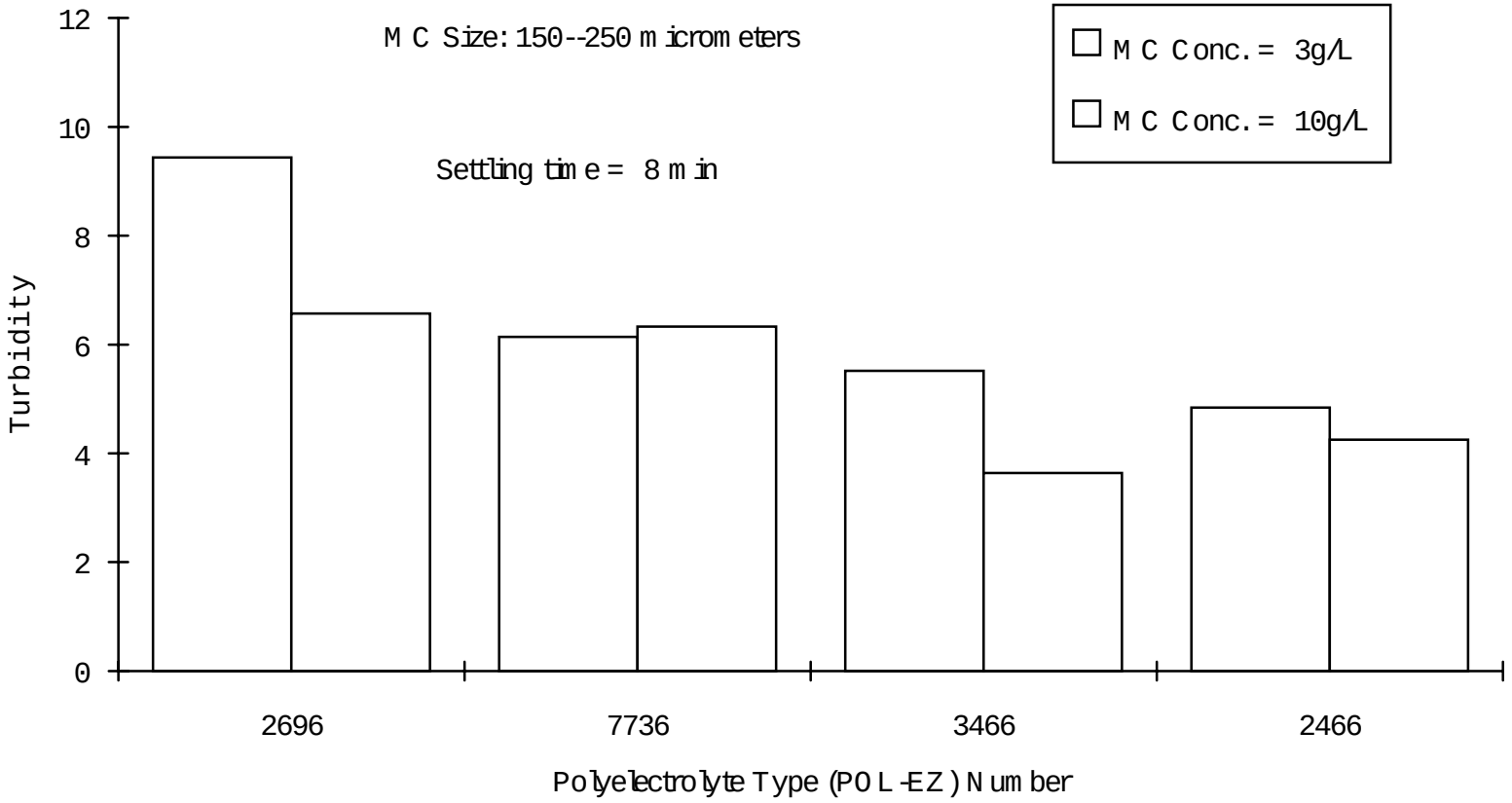
Settling Time: 3 and 8 minutes

Figure 4-27. Total Volatile Solids Distributions (Level-3; POL-EZ-2466)



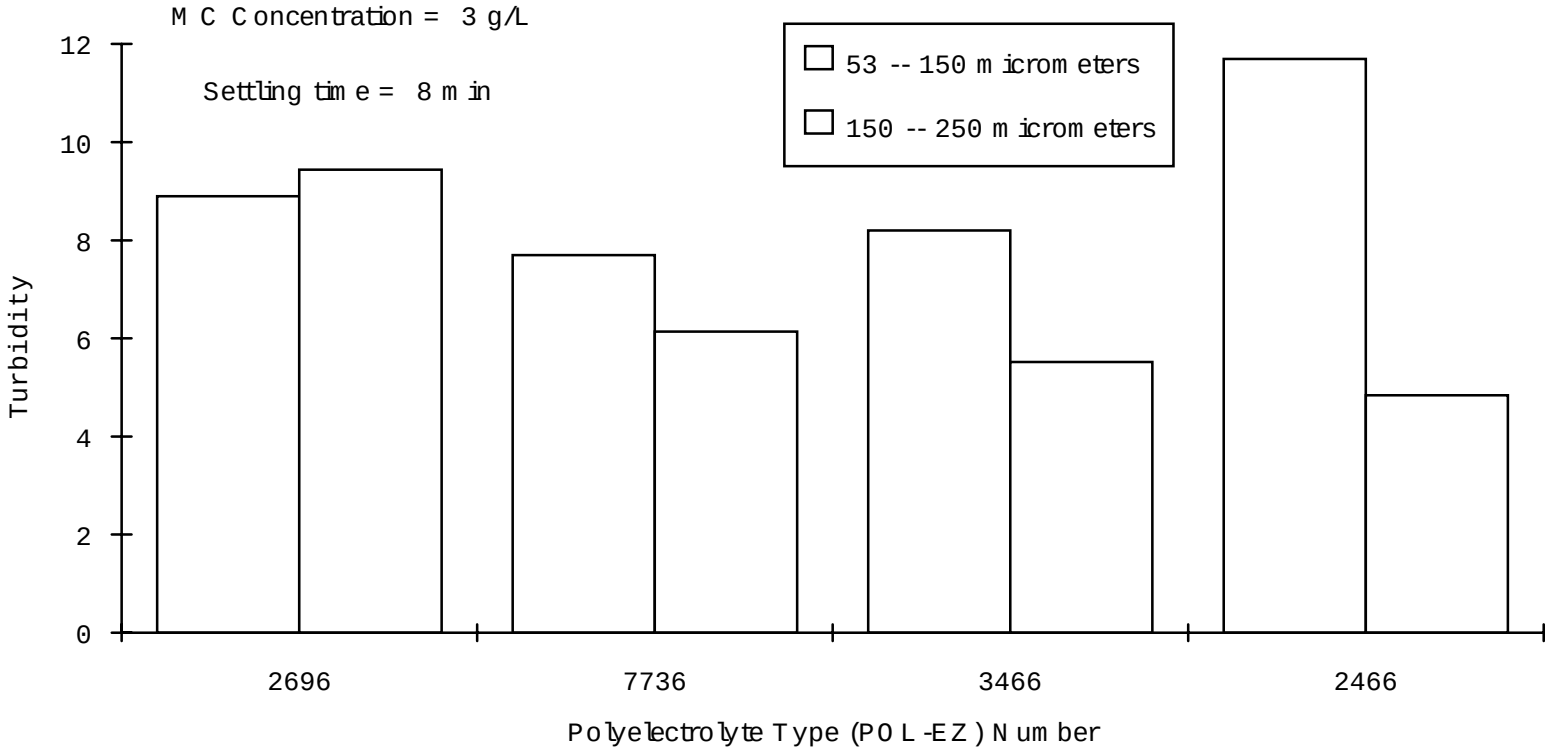
MC-1: MC Size Range = 53—150 µm; MC Concentration = 3 and 10 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4
Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-28. Turbidity for Different MC Concentrations (Small MC)



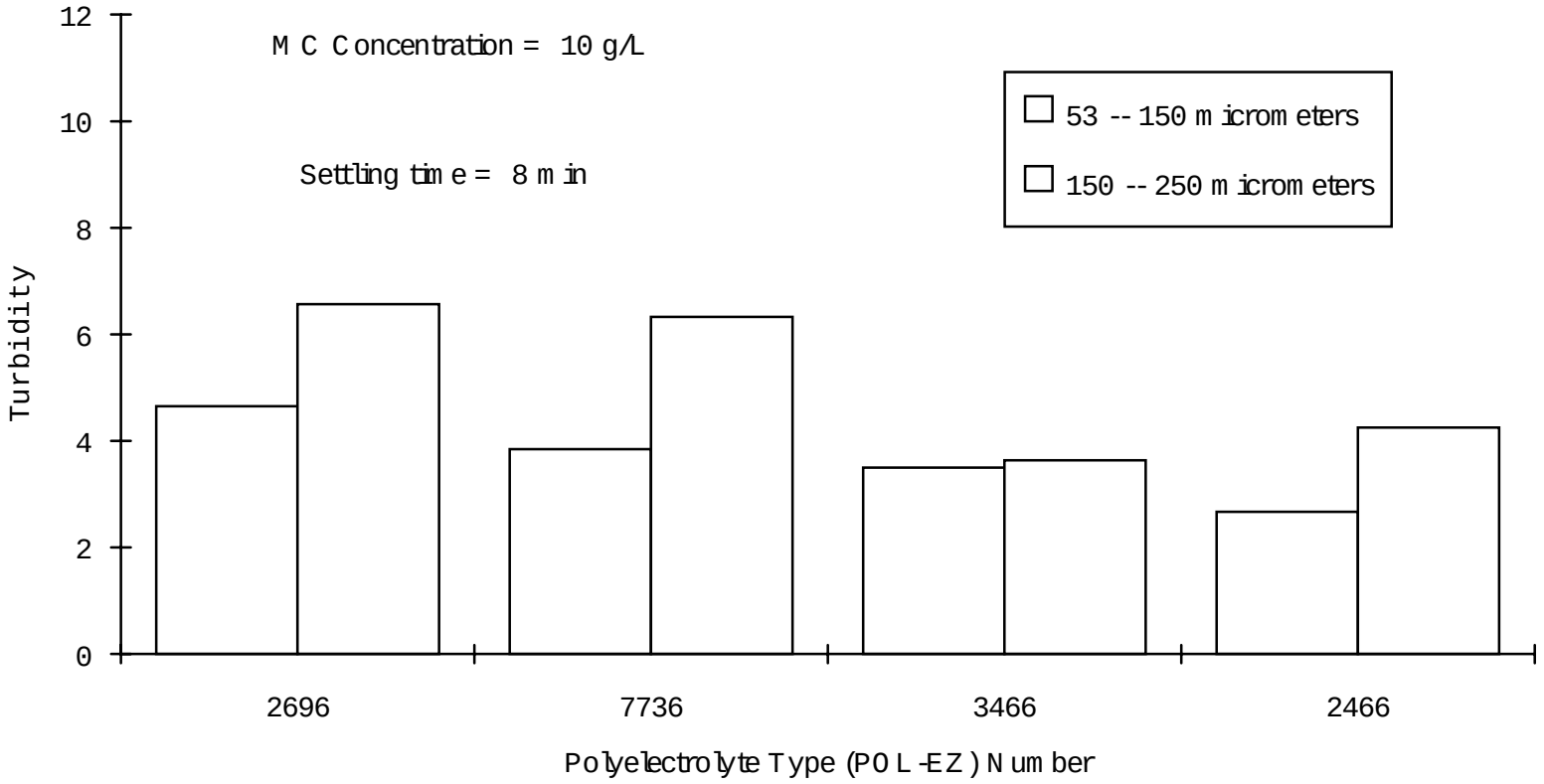
MC-1: MC Size Range = 150—250 µm; MC Concentration = 3 and 10 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4
Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-29. Turbidity for Different MC Concentrations (Large MC)



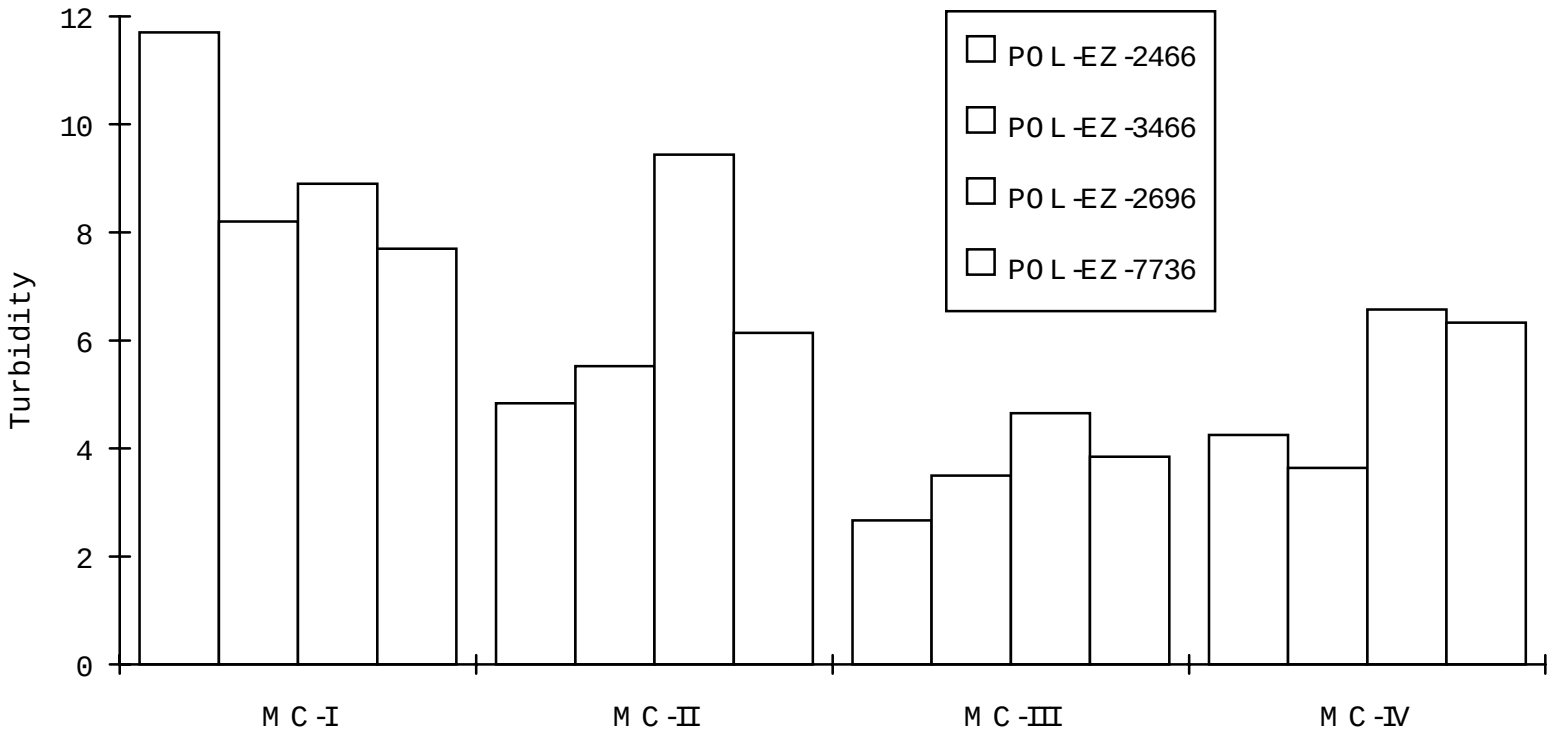
MC-1: MC Size Range = 53—150 µm and 150—250 µm; MC Concentration = 3 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4
Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-30. Turbidity for Different MC Sizes (Low MC Dosage)



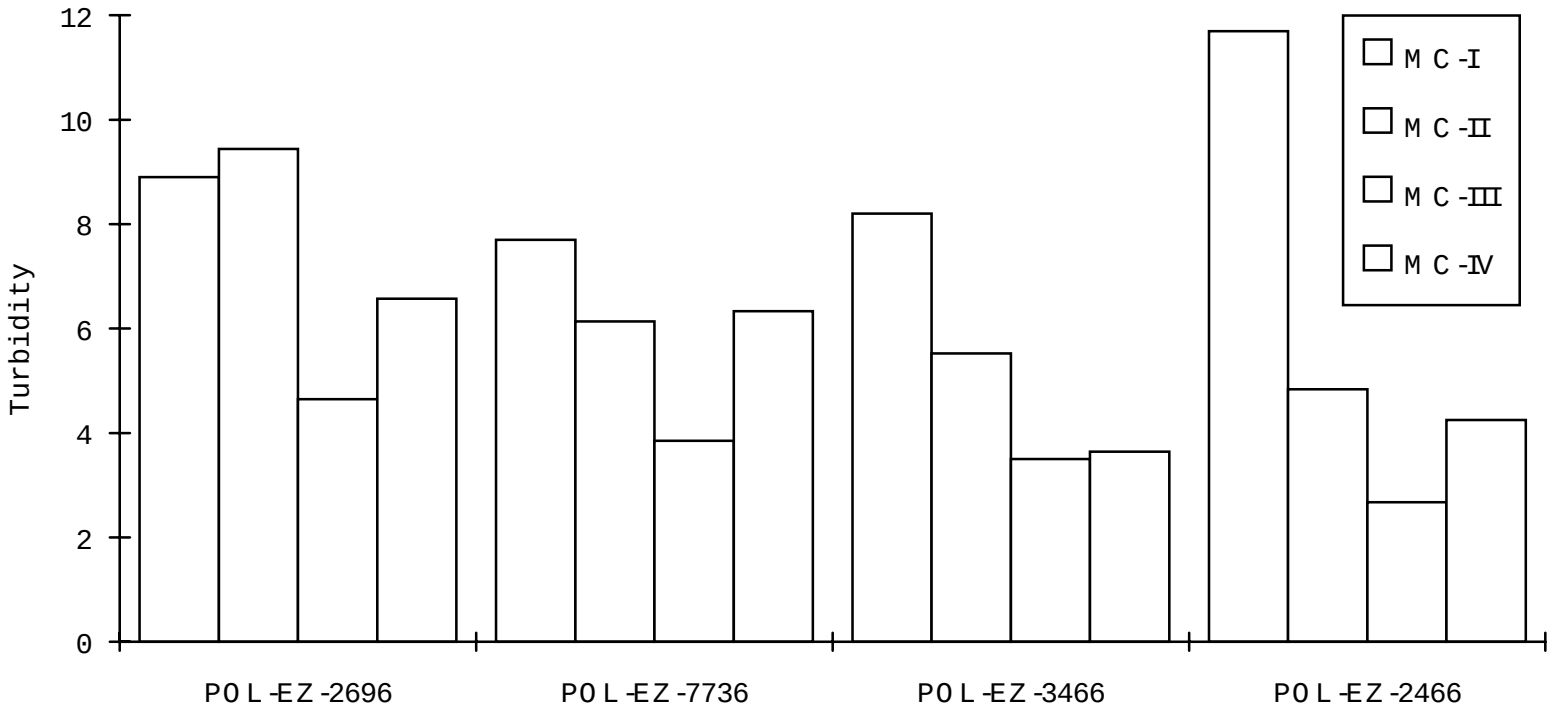
MC-1: MC Size Range = 53—150 µm and 150—250 µm; MC Concentration = 10 g/L
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4
Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-31. Turbidity for Different MC Sizes (High MC Dosage)



MC Group Identification, Size Range and Concentration in Table 3-8
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4
Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-32. Turbidity Summary for Confirmative Tests (by MC Group)



MC Group Identification, Size Range and Concentration in Table 3-8
E-1 (Electrolyte): Aluminum Sulfate Concentrations = 40 mg/L
Coagulant Aid (Polyelectrolyte) Identification in Table 3-4

Polyelectrolyte Concentration = 1 mg/L; Settling Time = 8 minutes

Figure 4-33. Turbidity Summary for Confirmative Tests (by Coagulant Aid Group)

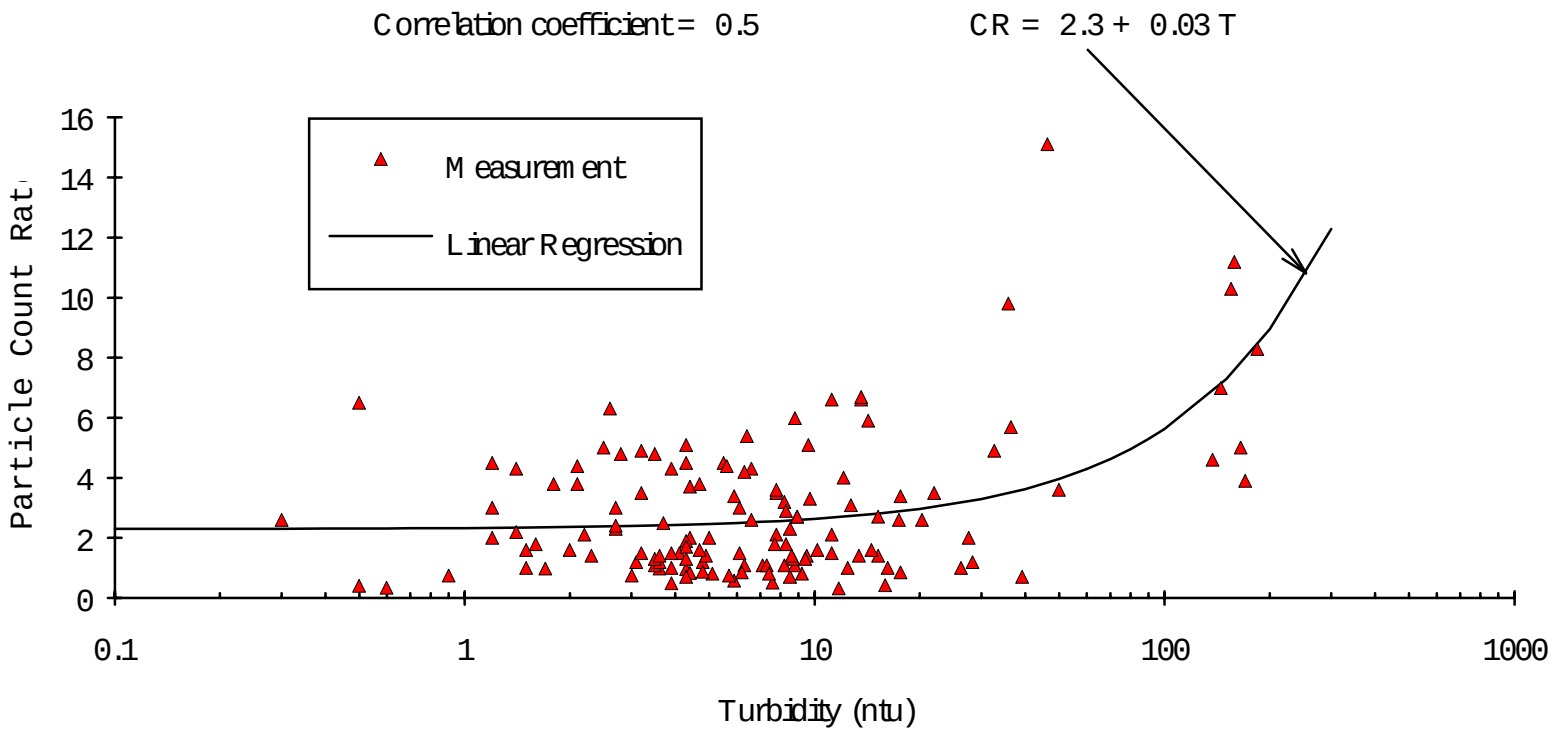


Figure 4-34. Correlation of Particle Count Rate and Turbidity

Chapter 5
Experimental Results: Combined Sewer Overflow

The purpose of this chapter is to examine the effectiveness of the MC process as a treatment technology for combined sewer overflows (CSO) (as was previously analyzed in the treatment for surface runoff). In developing this process, an experimental program was carried out. The analyses were based on past experience and information noted in Chapter 4. The experimental results are summarized hereby in four phases, namely, prescreening tests, effectiveness of MC process, control variable optimization, and response variable evaluation.

5.1 Prescreening Tests

Mixing Parameters. The mixing parameter setup for the CSO treatment is similar to those of the surface runoff tests as described in Chapter 4. For CSO samples, it was observed that flocs grow gradually within one to two minutes during slow mixing (flocculation). Along with the growth of flocs, the mixing rate should vary from 60 rpm at the beginning to 20 rpm at the latter part of mixing process in order to reduce shear stress and avoid floc break down. The total mixing time is less than two minutes.

Table 5-1 presents a summary of experimental settings to be used in subsequent tests in control variable optimization and response variable evaluation. These settings were based on prescreening tests.

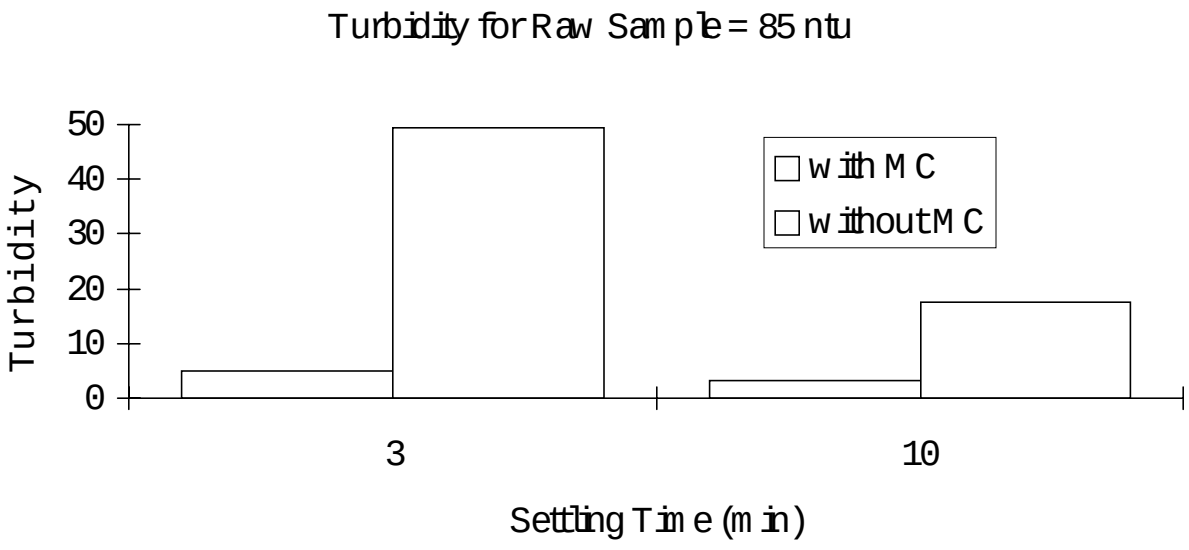
5.2 Effect of the MC

The effect of the MC weighted coagulation was evaluated via turbidity indicator as well as particle size distribution at the pre- and post-jar test of raw and supernatant samples, respectively. Figure 5-1 presents results of turbidity versus settling time with and without the use of an MC. With the MC process, the turbidity was reduced from 85 ntu (for the raw sample) to 5.0 and 3.1 NTU at the 3- and 10-minute settling times, respectively. At the 3- and 10-minute settling times, the turbidity without MC is 10 and 5.6 times that of the turbidity levels with MC, respectively. Thus, the MC treatment process is effective for removal of turbidity in CSO samples.

Figures 5-2 and 5-3 illustrate cumulative and non-cumulative volume distributions versus particle size before and after the MC treatment process, respectively. For the raw sample (before treatment), the measurable range of particle size was from 0.5 to 60 μm with 93% particles larger than 2 μm in size. After the MC treatment, the particles in the supernatant of the sample were found to be smaller than 2 μm, thus indicating that particles larger than 2 μm in the raw sample were totally removed.

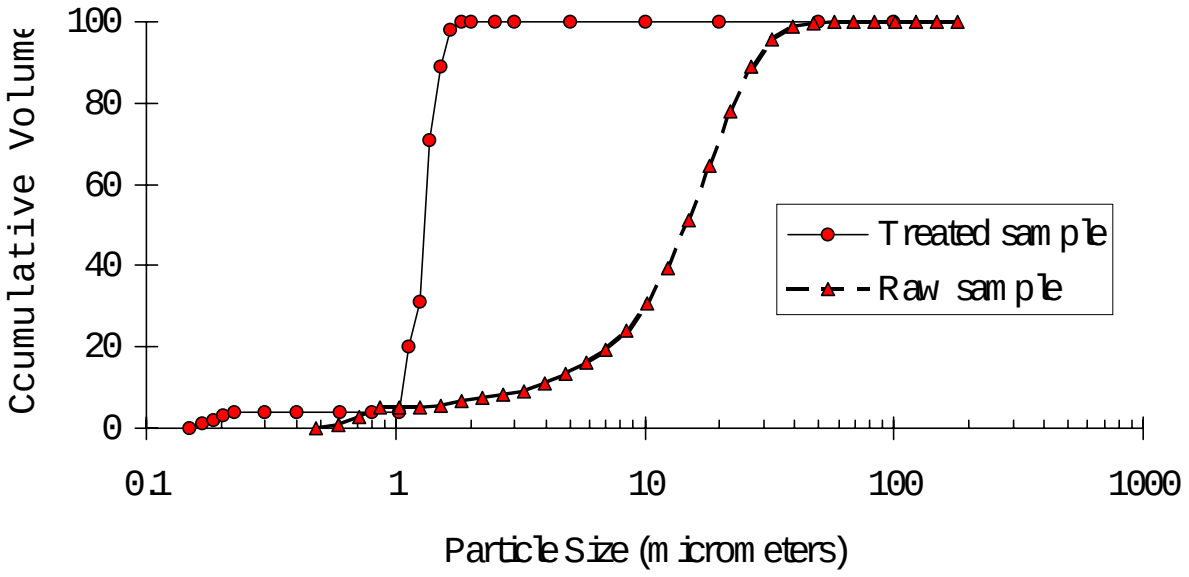
Table 5-1. Summary of Experimental Settings for CSO Treatment

Parameter	Value
Rapid mixing rate -- stage-1	150 rpm
Rapid mixing duration -- stage-1	10 sec
Rapid mixing rate -- stage-2	100 rpm
Rapid mixing duration -- stage-2	10 sec
Slow mixing (Flocculation)rate	20—60 rpm
Flocculation mixing duration	1—1.5 min
MC concentration	1—7 g/L
MC size range - 1	53—75 μm
MC size range - 2	150—250 μm
Settling time	1—20 min
Ferric chloride concentration	10—100 mg/L(as Fe^{+++})
Coagulant aid (polyelectrolyte) concentration	0.5—15 mg/L



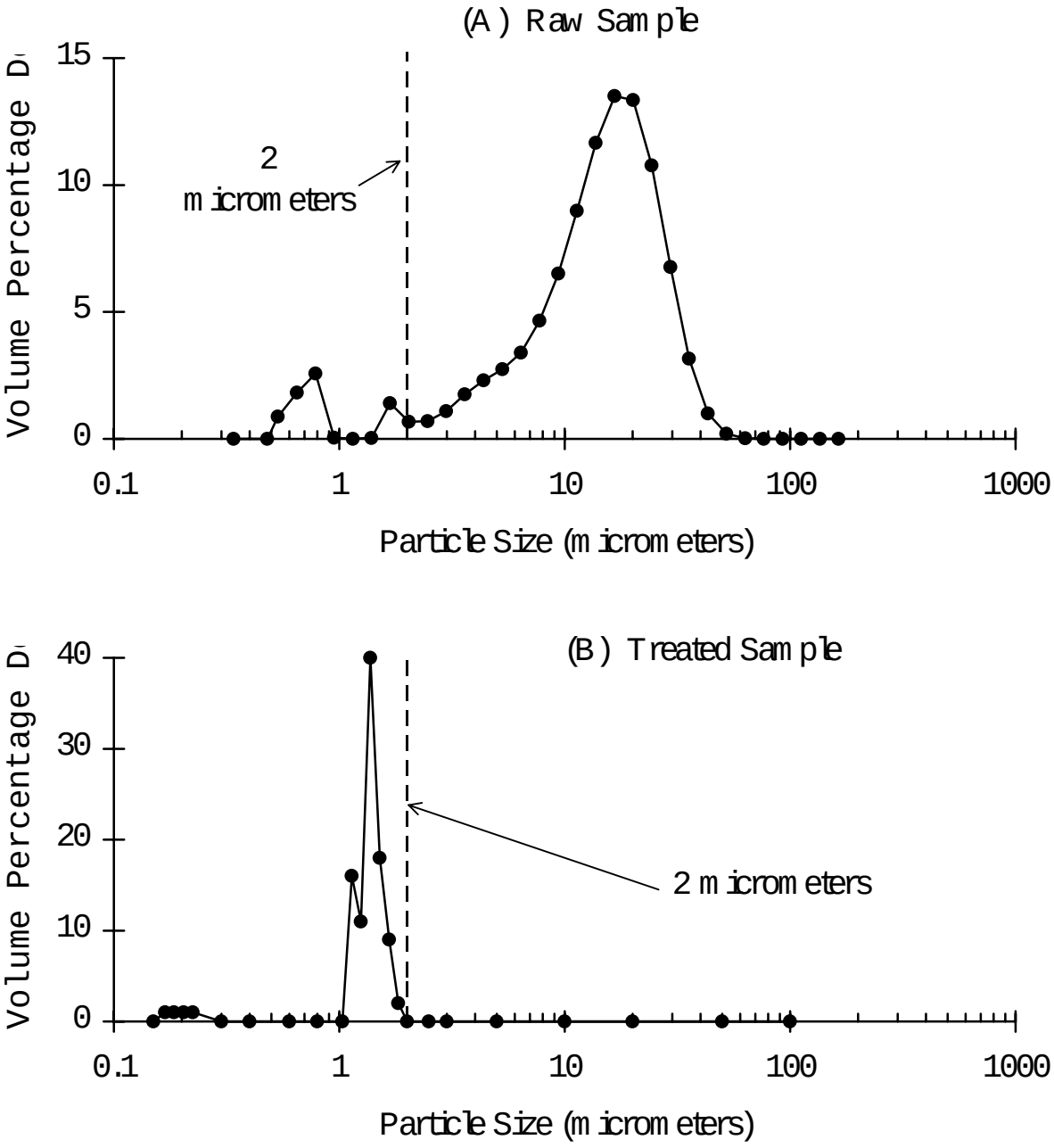
MC-5: MC Size Range = 53—75 µm; MC Concentration = 3g/L
E-2: Ferric Chloride Concentration = 40 mg/L(as Fe^{+++})
PE-5: Polyelectolyte 309C Concentration = 2 mg/L

Figure 5-1. Effect of MC



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L(as Fe^{+++})
PE-5: Polyelectolyte 309C Concentration = 1.5 mg/L

Figure 5-2. Particle Sizes of Raw and Treated Samples (Cumulative)



MC-5: MC Size Range = 53—75 μm; MC Concentration = 3g/L
E-2: Ferric Chloride Concentration = 40 mg/L(as Fe^{+++})
PE-5: Polyelectolyte 309C Concentration = 1.5 mg/L

Figure 5-3. Particle Sizes of Raw and Treated Samples (Distributions)

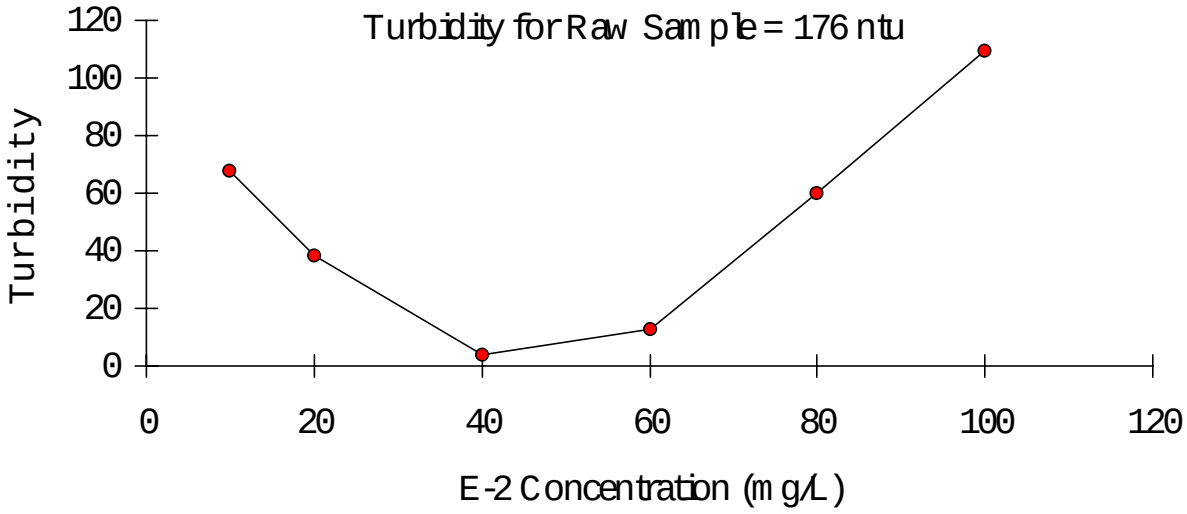
5.3 Control Variable Determination

In the determination of the effectiveness of the MC process, turbidity and particle count rate were employed as primary and secondary indicators, respectively. Six parameters, including coagulant concentration, coagulant aid concentration, MC size, MC concentration and settling time were identified as control variables. Results from each of the control variables with respect to the turbidity and particle count rate are presented in this section.

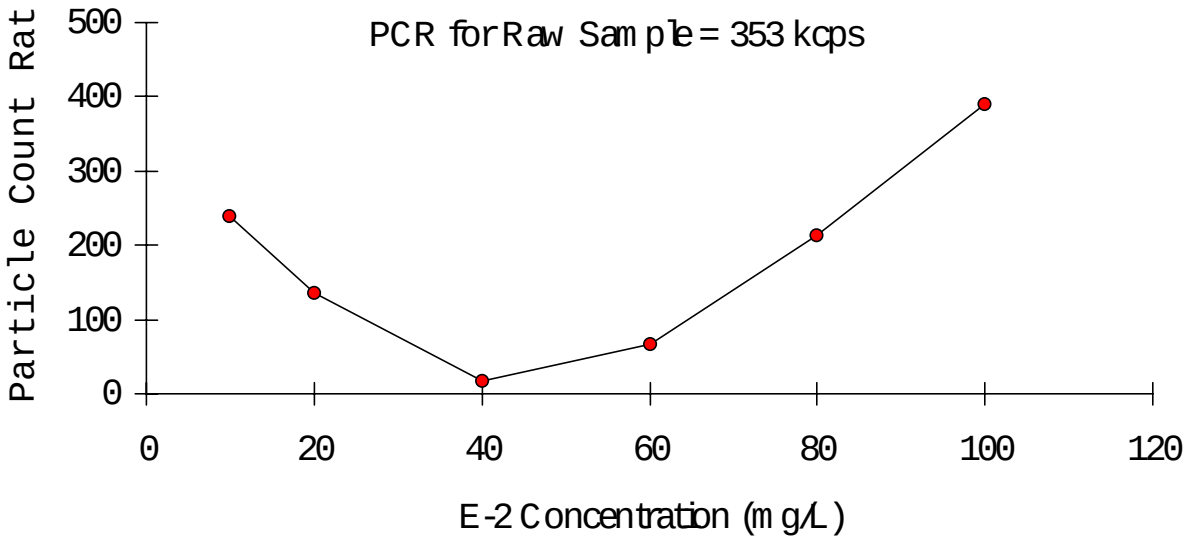
Coagulant Concentration

Turbidity and particle count rate of post treatment supernatant samples with respect to coagulant concentration are illustrated in Figure 5-4 (A) and (B), respectively. It can be seen that the optimal coagulant concentration is 40 mg/L for both turbidity and particle count rate indicators. The removal rates are 98% for turbidity and 95% for particle count rate at the optimal coagulant concentration. These results are confirmed in Figure 5-5 that also shows that the optimal dosage for coagulant is 40 mg/L. Although the raw samples for these two tests are from different batches, the results are similar.

It is of interest to note that the distribution trends for turbidity and particle count rate are very similar. Figure 5-6 indicates a linear relationship between these two parameters.



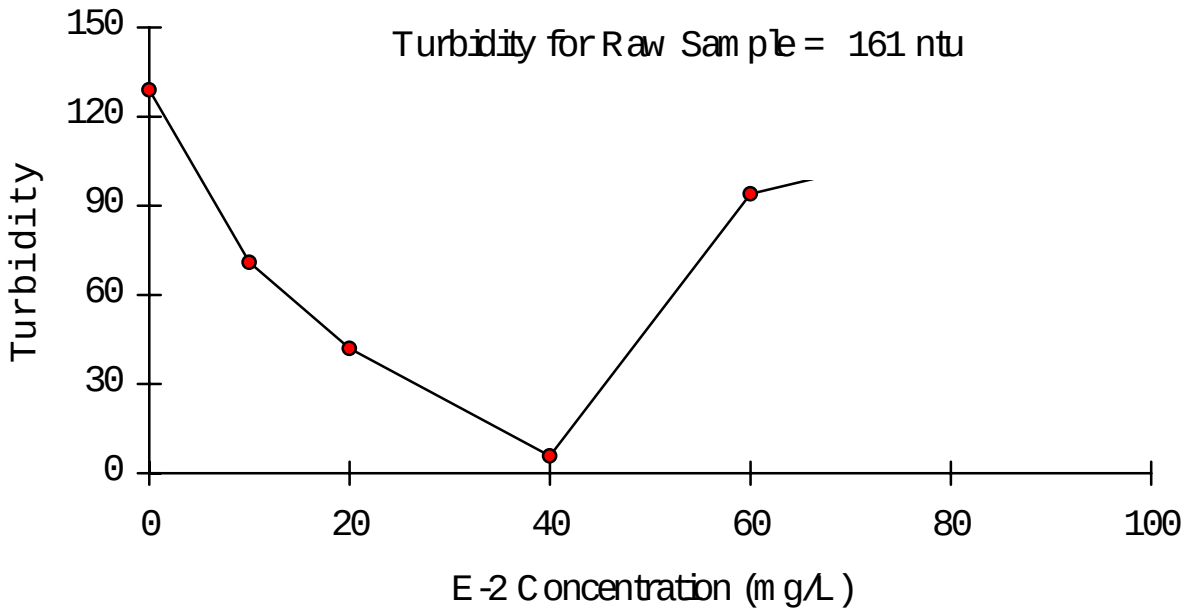
(A) By Turbidity Indicator



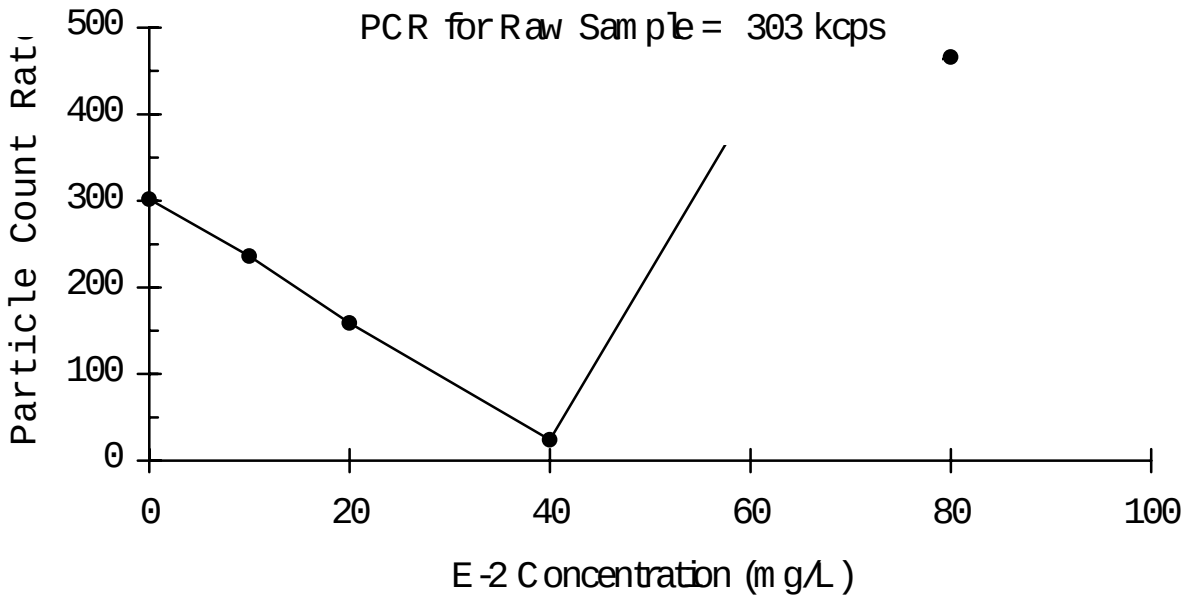
(B) By Particle Count Rate Indicator

MC-5: MC Size Range = 53—75 µm; MC Concentration = 3g/L
E-2: Ferric Chloride Concentration Range: 10—100 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 2 mg/L
Settling Time = 3 min

Figure 5-4. Coagulant Concentration Selection (Test-1)



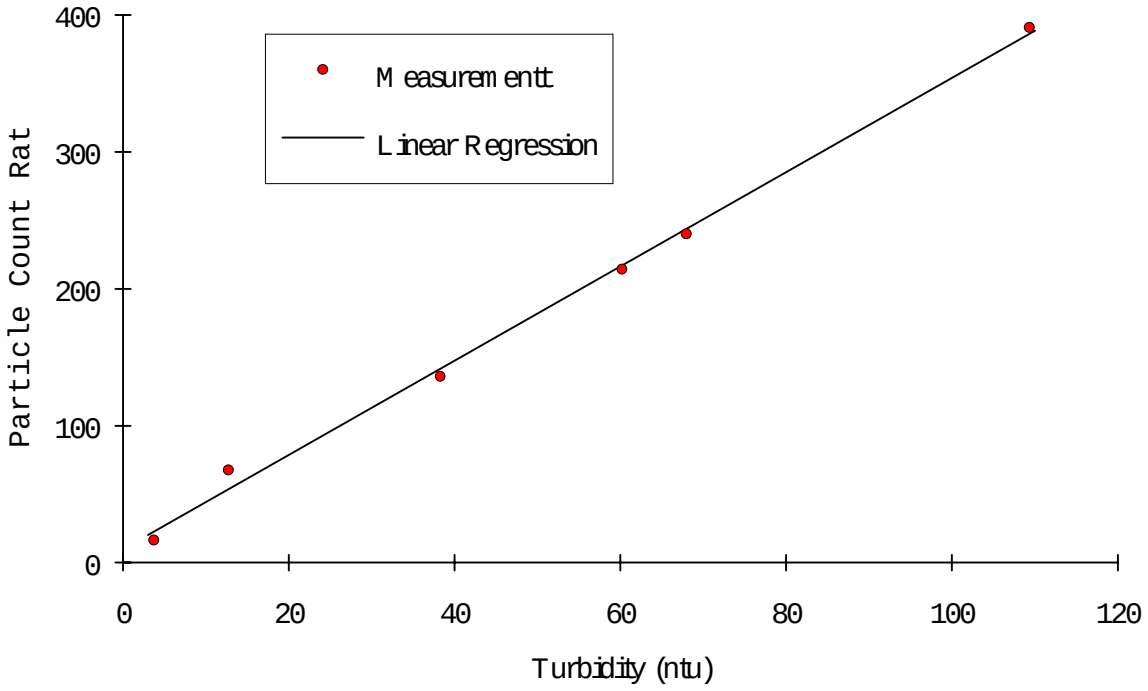
(A) By Turbidity Indicator



(B) By Particle Count Rate Indicator

MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration Range: 0—80 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 1 mg/L
Settling Time = 3 min

Figure 5-5. Coagulant Concentration Selection (Test-2)



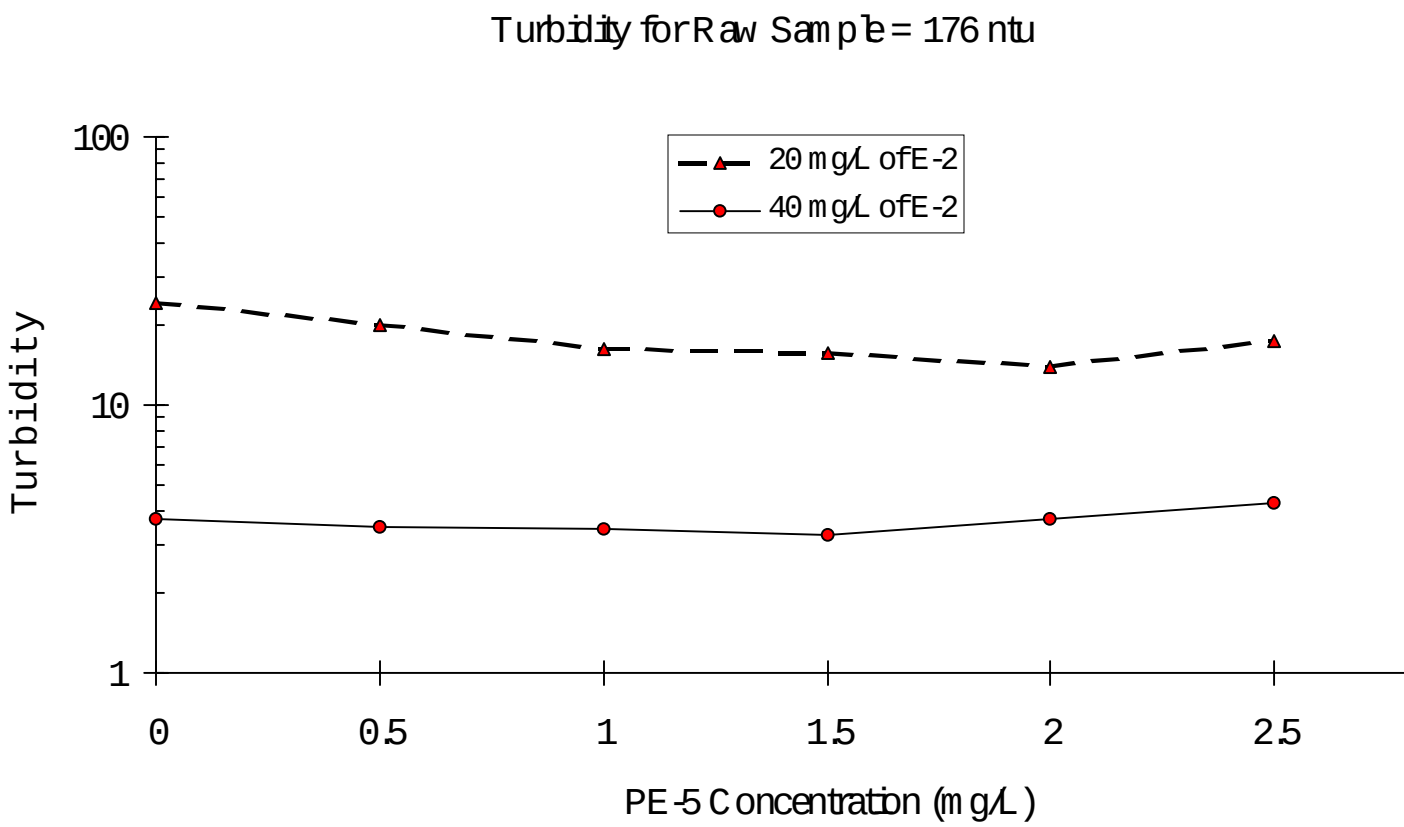
MC-5: MC Size Range = 53—75 µm; MC Concentration = 3g/L
E-2: Ferric Chloride Concentration Range: 2—110 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 2 mg/L
Settling Time = 3 min

Figure 5-6. Particle Count Rate Versus Turbidity

Coagulant Aid Concentration

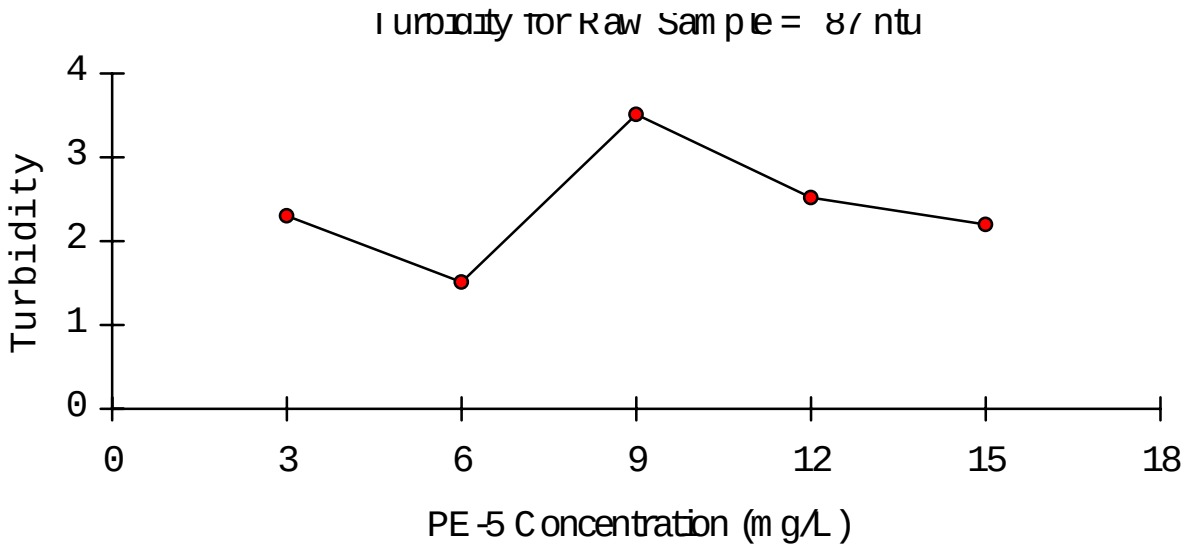
Figure 5-7 presents a comparison of the turbidity distribution versus coagulant aid concentration for two coagulant concentrations (20 and 40 mg/L). The coagulant aid concentration appears to have less influence on final turbidity in low dosages (ranged 0—2.5 mg/L) for both coagulant concentrations.

For higher coagulant aid concentration ranged 3—15 mg/L, 6 mg/L dosage resulted lowest turbidity as illustrated in Figure 5-8.



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectrolyte 309C; Settling Time = 3 min

Figure 5-7. Polyelectrolyte Concentration Selection (Low Dose)



MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectrolyte 309C; Settling Time = 3 min

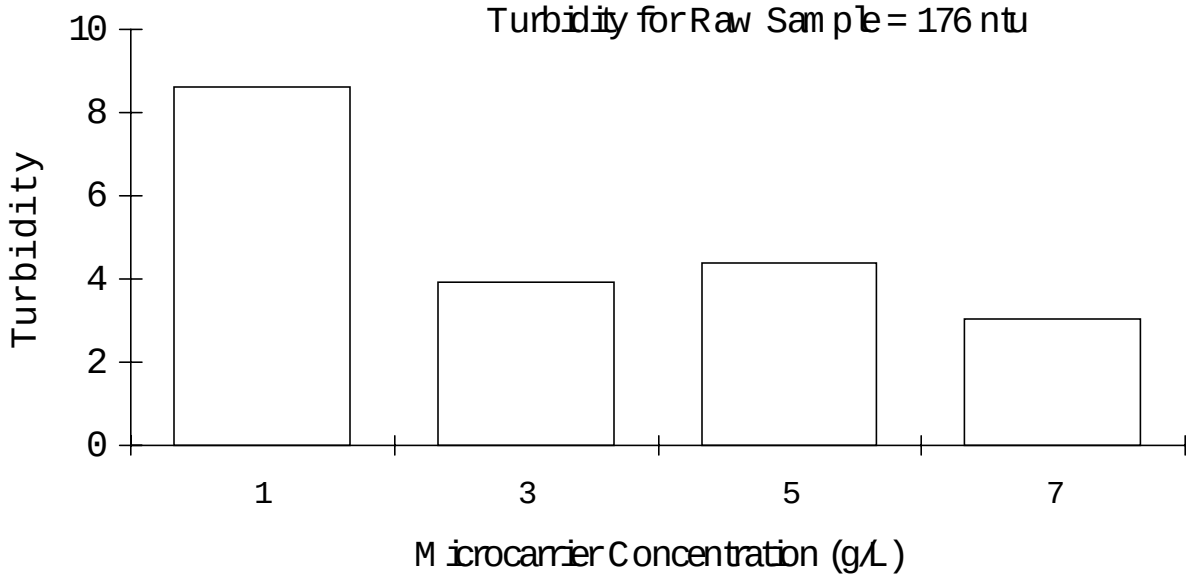
Figure 5-8. Polyelectrolyte Concentration Selection (High Dose)

MC Concentration

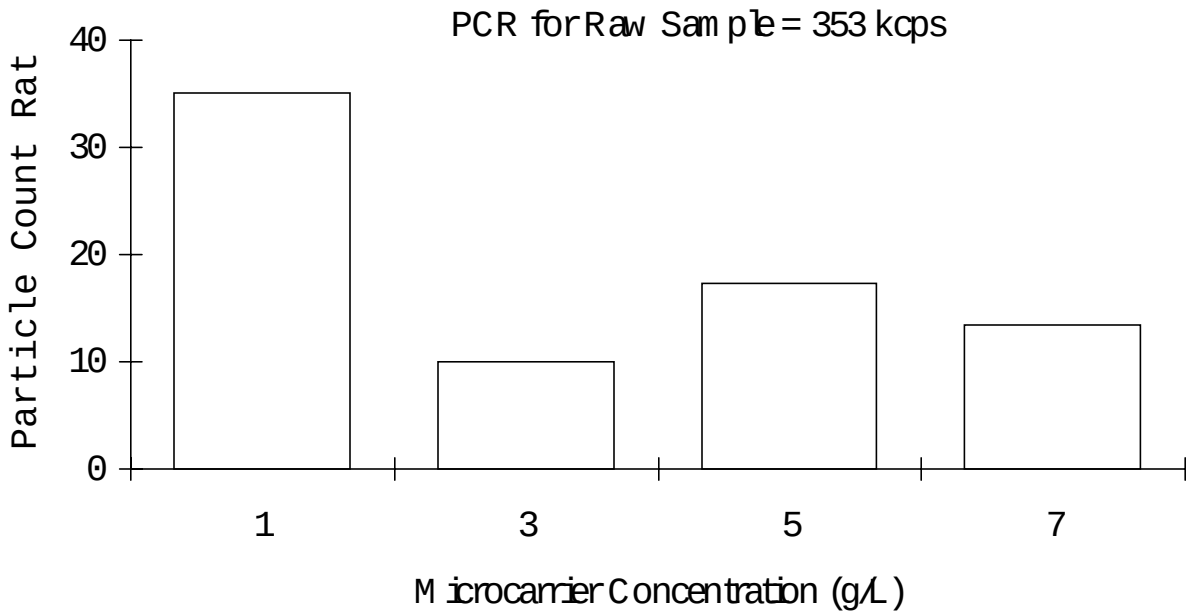
Four different MC concentrations, ranging between 1 and 7 g/L were utilized to determine an optimal value. Figures 5-9(A) and (B) illustrate turbidity and particle count rate distributions versus four different MC concentrations, respectively. In Figure (A), a sharp decrease in turbidity was observed for MC concentrations between 1 and 3 g/L, with slight fluctuations at 5 and 7 g/L of MC. Although 7 g/L MC yields the lowest turbidity, the improvement is only 23% greater compared with 3 g/L MC while the MC concentration level is increased by 133%. Using particle count rate as an indicator in Figure (B), 3 g/L MC appears to yield the lowest result. Based on the results of both turbidity and particle count rate, a 3-g/L of MC was selected as the optimal concentration.

MC Size

Five different size ranges for MCs were employed in the tests. Turbidity and particle count rate versus the five different MC sizes, along with one sample without MC, are shown in Figure 5-10 (A) and (B), respectively. It can be seen that the size range from 53 to 75 μm yields the best results for both turbidity and particle count rate. Thus, this size range was selected as the optimal MC size.



(A) By Turbidity Indicator

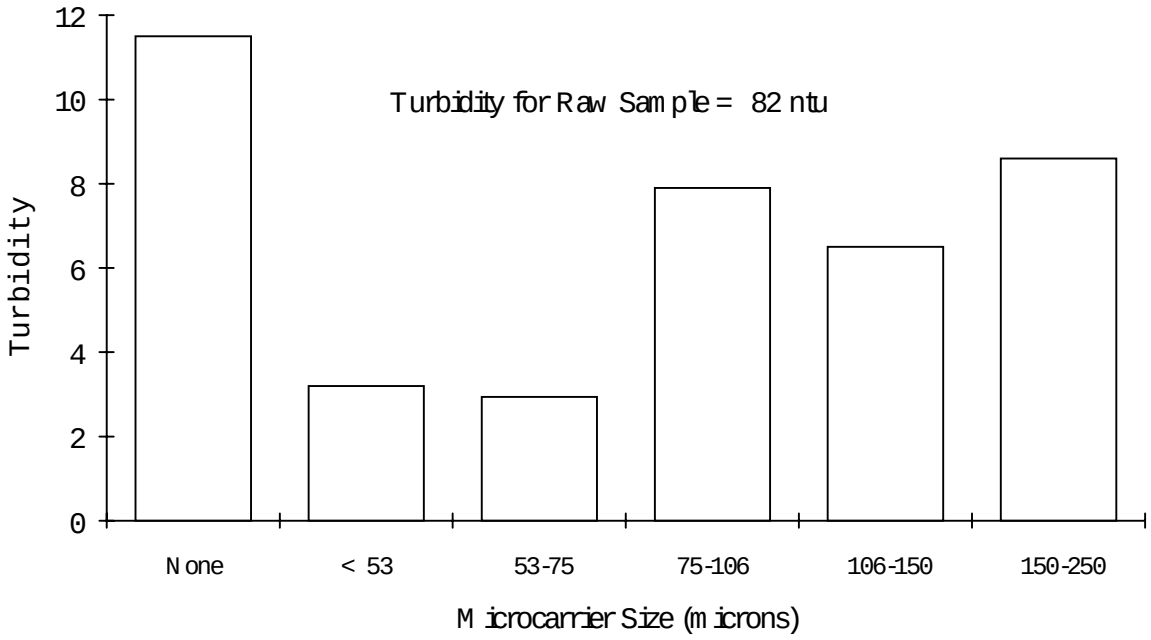


(B) By Particle Count Rate Indicator

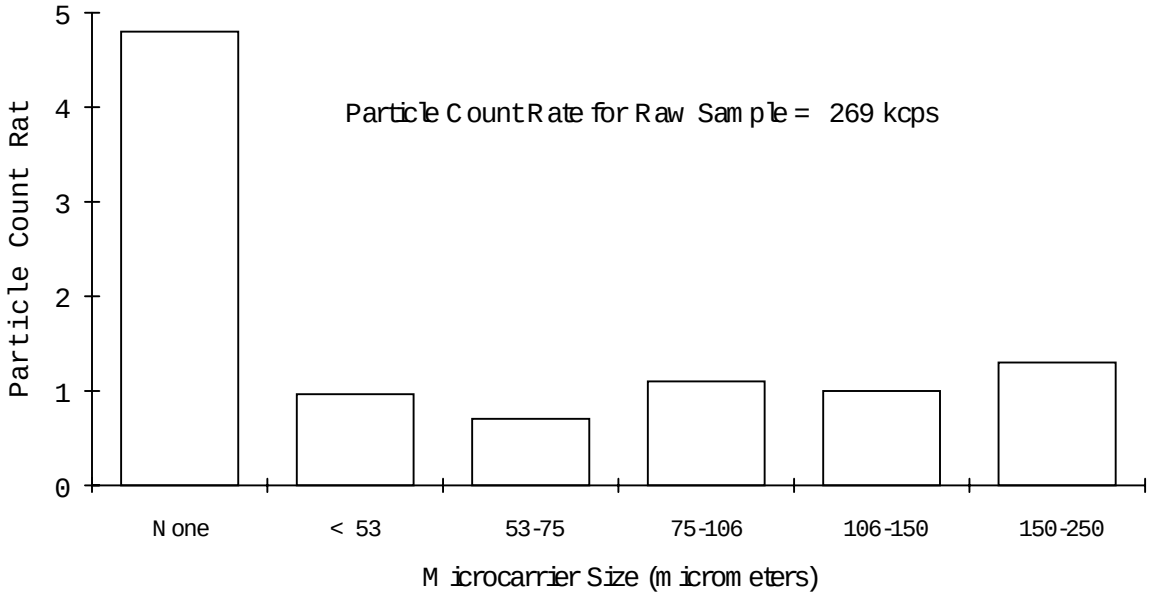
MC Size Range = 53—75 μm;

E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++};
PE-5: Polyelectolyte 309C Concentration = 2 mg/L

Figure 5-9. MC Concentration Selection



(A) By Turbidity Indicator



(B) By Particle Count Rate Indicator

MC Concentration = 3g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++};
PE-5: Polyelectolyte 309C Concentration = 2 mg/L

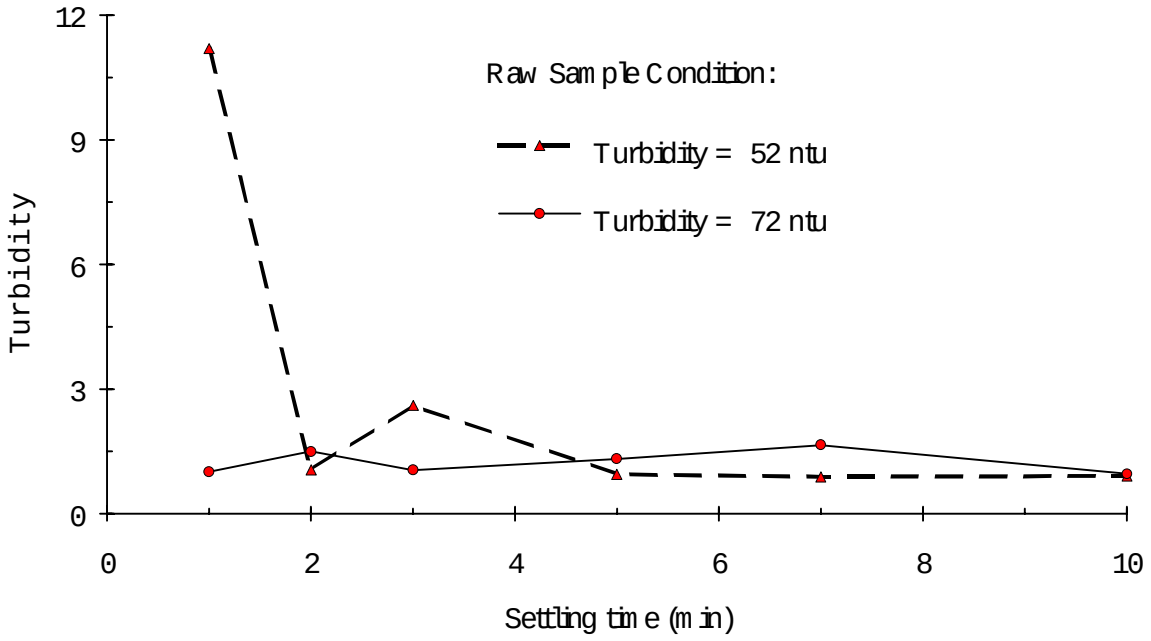
Figure 5-10. MC Size Selection

Settling Time

Settling time required is one of the key factors in the coagulation-flocculation treatment process since settling kinetics governs the treatment efficiency, duration, and thus the size of the treatment facility. The MC process appears to provide very efficient settling characteristics for CSO treatment.

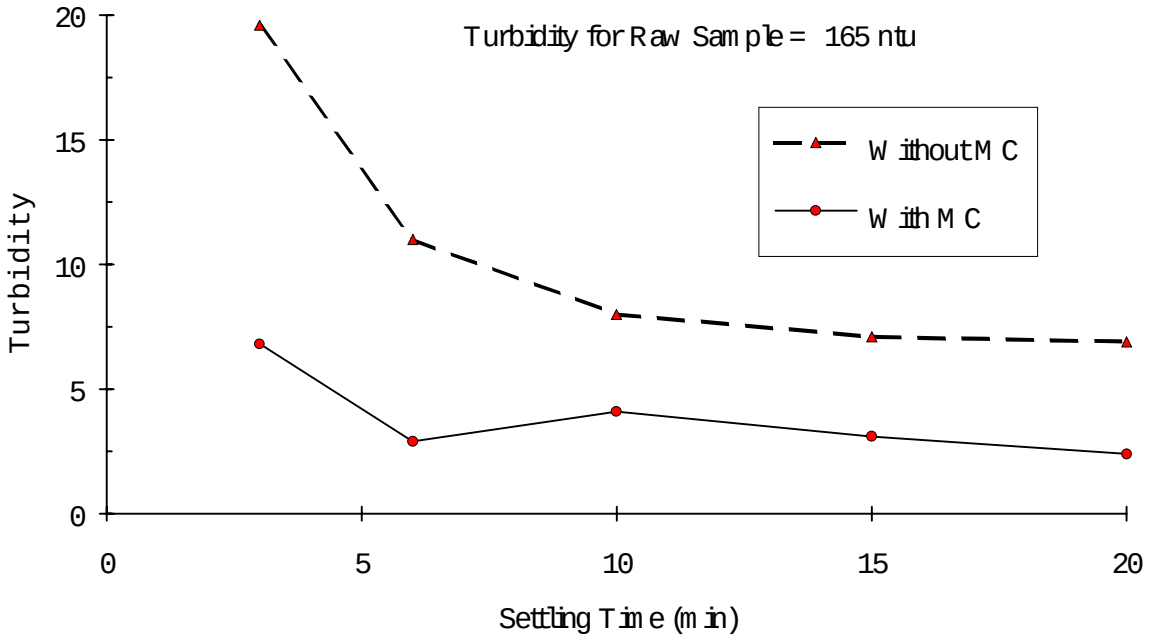
Figure 5-11 shows results of turbidity versus settling time from 1 to 10 minutes. In both tests, the post-treatment turbidity was reduced to 1.3 ntu with a minor fluctuation within a two-minute settling period. The average turbidity removal rate was 98% over the settling duration of 2 to 10 minutes.

Figure 5-12 illustrates a comparison of settling kinetics with and without the use of MC, respectively. In this test, it can be seen that the MC process enhances both short-term (3 minutes) and long term (20 minutes) settling characteristics.



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 6 mg/L

Figure 5-11. Turbidity Versus Settling Time with Optimal Condition



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 1 mg/L

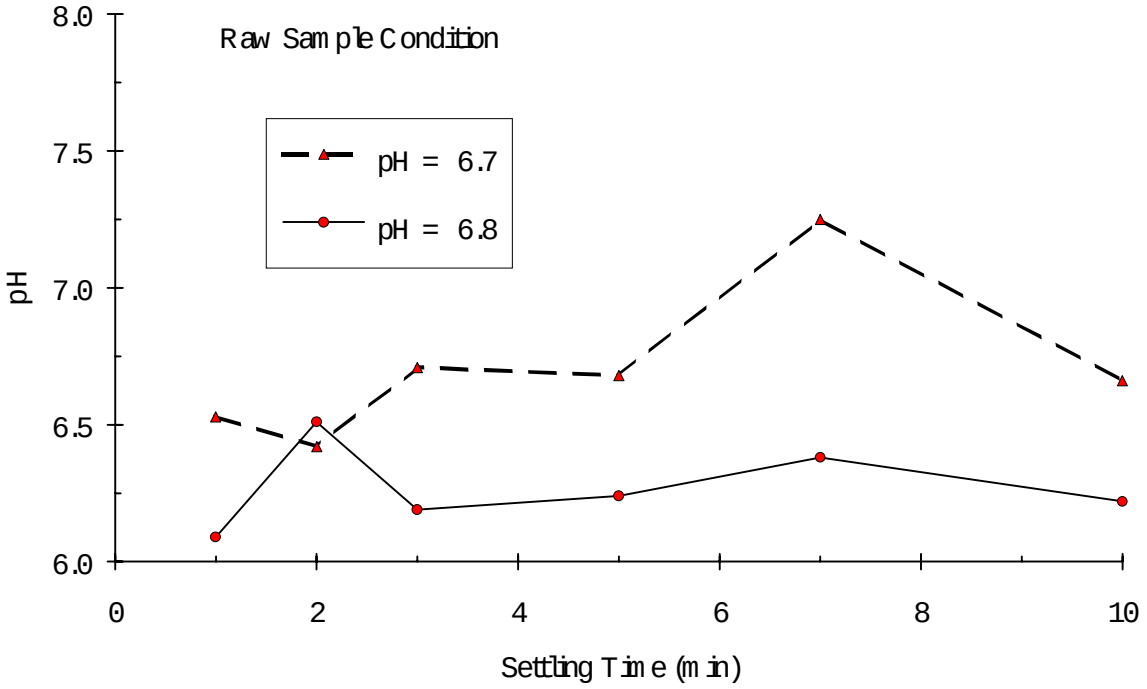
Figure 5-12. Turbidity Versus Settling Time

5.4 Response Variable Evaluation

During the CSO treatment stage, the response variables included the following parameters: turbidity, particle count rate, pH, suspended solids, total solids, total volatile solids, particle size distribution, total organic carbon, total inorganic carbon, fecal coliform, and zeta potential. Among these parameters, turbidity and particle count rate have been presented in Section 5.3. In this section, the results of the other response variables are evaluated.

pH

Figure 5-13 illustrates pH distributions for two different raw samples along with settling time from 1 to 10 minutes. It can be seen that under the optimal control variable setup, all pH values are within the range of 6.0 to 7.5.

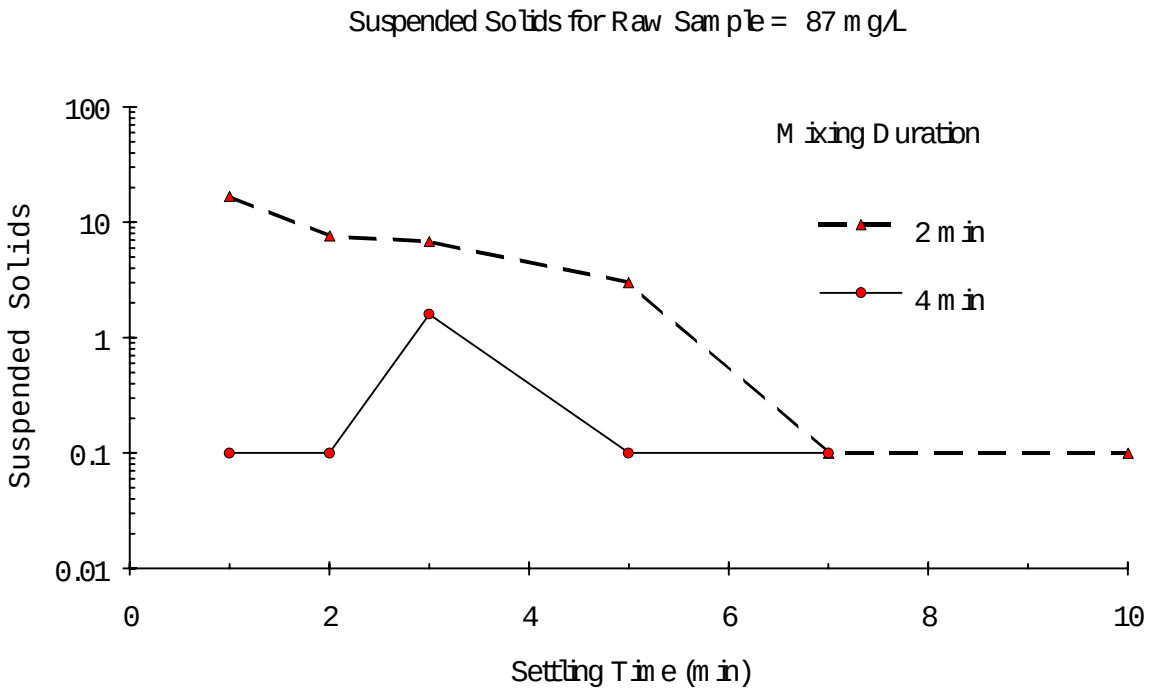


MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 6 mg/L

Figure 5-13. pH Versus Settling Time with Optimal Condition

Suspended Solids

Figure 5-14 illustrates suspended solids versus settling time with two different mixing periods, i.e., 2 and 4 minutes, respectively. Excellent results for both samples were found to be less than 10 mg/L with the exception of one sample with a one-minute settling time. Suspended solids were found to be less than 2 mg/L with a 4-minute mixing time. The removal efficiency is 97% after 2 minutes of mixing (average from 3 to 10 minute settling) and 99.5% after 4 minute of mixing (average from 1 to 7 minute settling), respectively. For both tests, the supernatant suspended solids reach the lower measurement limit (0.1 mg/L) after 7 minutes of settling.



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L

E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}

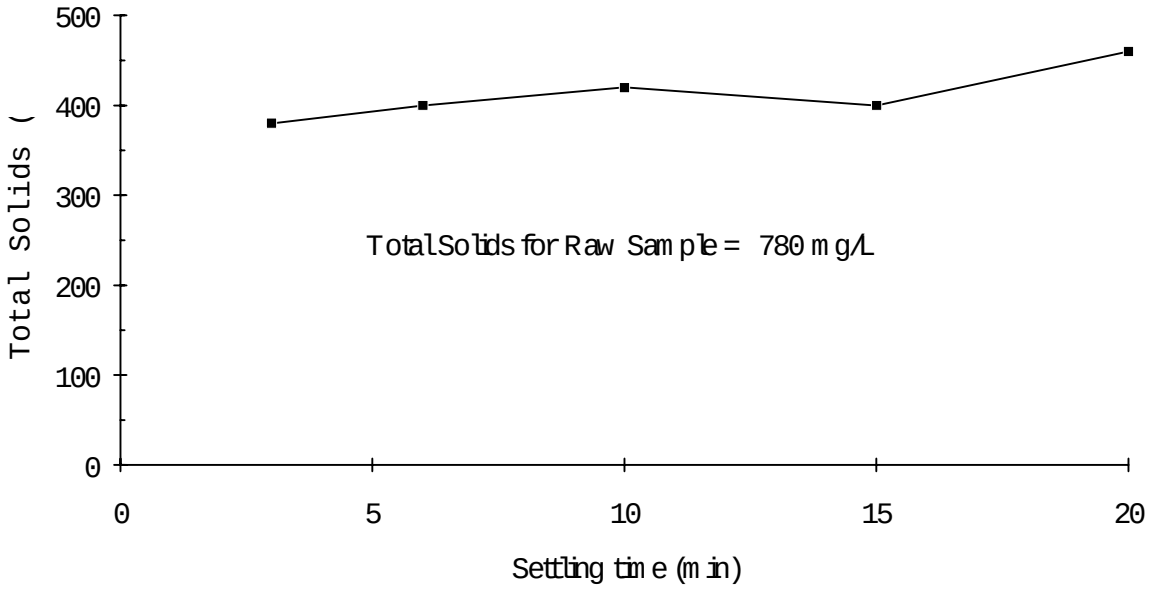
PE-5: Polyelectolyte 309C Concentration = 6 mg/L

Figure 5-14. Suspended Solids Versus Settling Time

Total Solids

The MC process was designed to remove suspended solids and any contaminants associated with suspended solids. Therefore, if suspended solids are the major component in the total solids, as

for surface runoff treatment, then the total solids removal could be effective. However, if dissolved solids were the major component in total solids, the total solids removal efficiency would be significantly limited by the content of organic portion of suspended solids in the raw sample. For the CSO treatment, total solids removal rates are approximately 50% as illustrated in Figure 5-15.

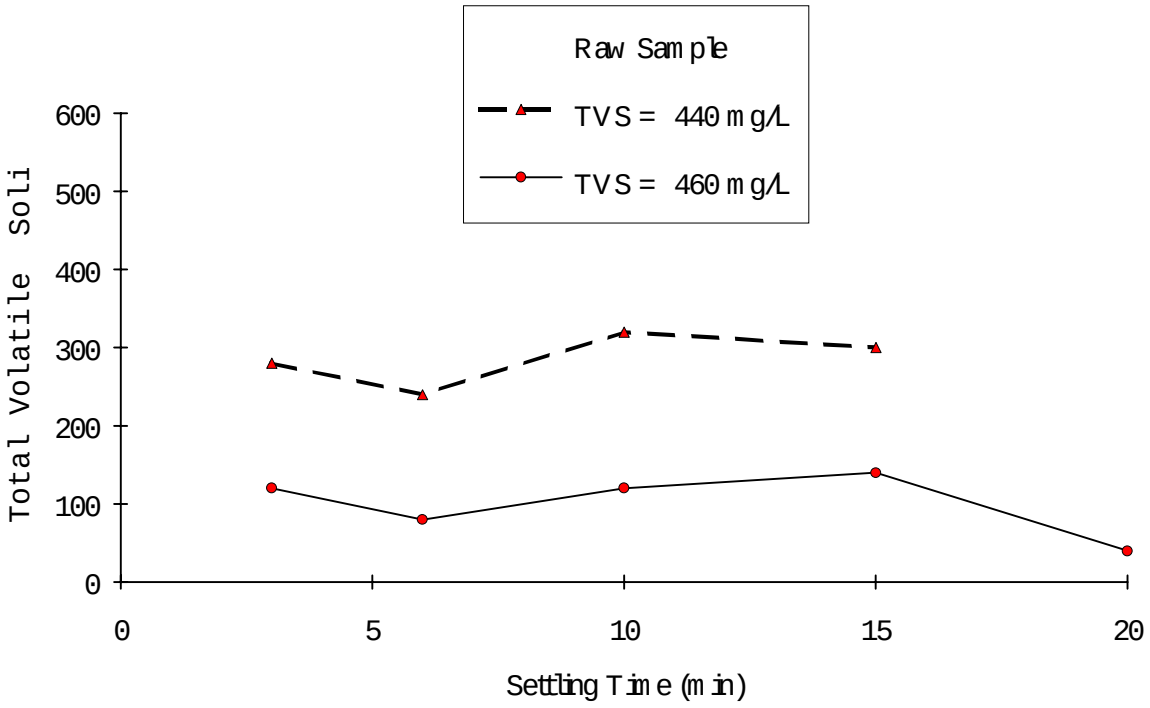


MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 1 mg/L

Figure 5-15. Total Solids Versus Settling Time

Total Volatile Solids

As with total solids removal, the total volatile solids removal efficiency was also limited by the content of organic portion of suspended solids in the raw samples. It was found that the total volatile solids removal rate was in the range of 60% to 80%. The results of the two sets of jar tests with similar conditions but different sample batches are illustrated in Figure 5-16.

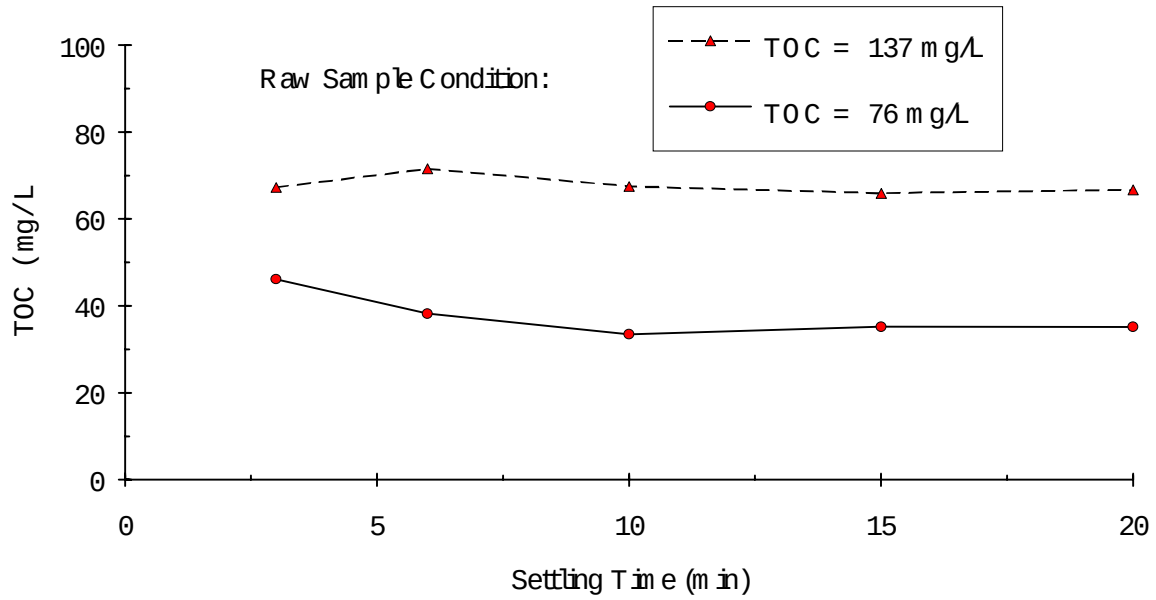


MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 1 mg/L

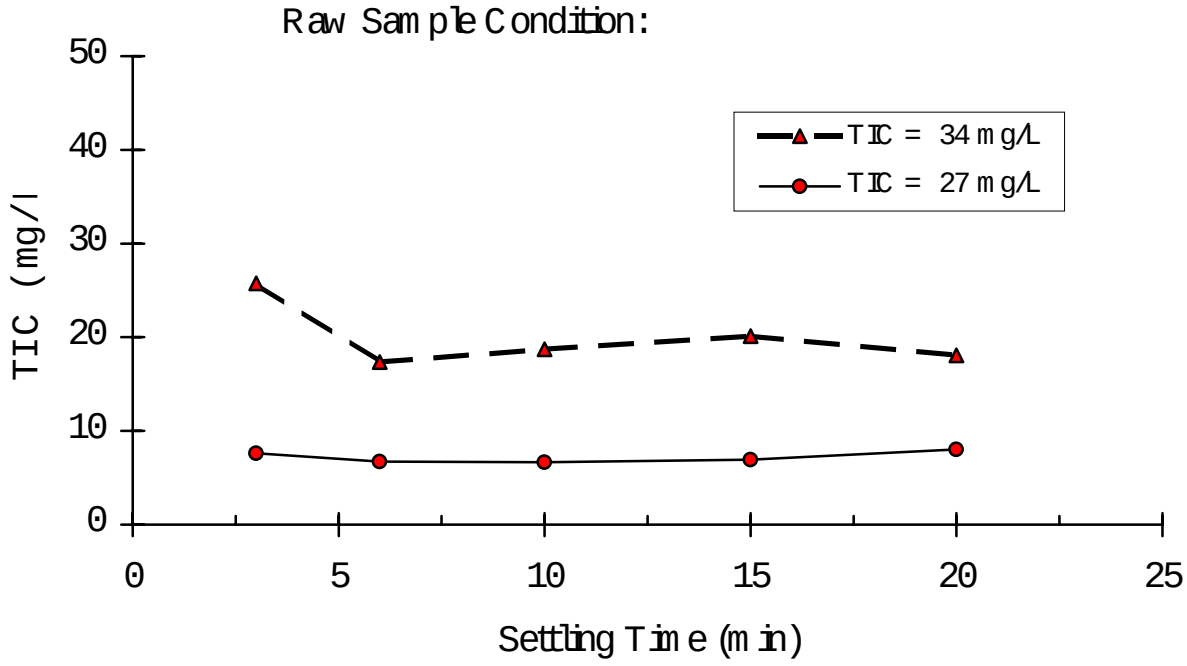
Figure 5-16. Total Volatile Solids Versus Settling Time

Total Organic and Inorganic Carbon

Figures 5-17 (A) and (B) show the results of total organic and inorganic carbon with respect to settling time for two different raw samples. It appears that a 3-minute settling time would be sufficient to achieve a stable condition. It was observed that the average total organic and inorganic carbon removal rates over the settling times from 3 to 20 minutes are approximately 50 and 70 percent, respectively. It was found that these removal rates remained the same although the post-treatment total organic and inorganic carbon values varied for different raw sample conditions. These removal rates were limited by the fact that only total organic carbon associated with the suspended solids were removed while total organic carbon in the dissolved format still remained in the solution after the MC process treatment. Figure 5-18 illustrates comparison results from two different mixing durations, 2- and 4-minute, respectively. It appears that the influence of mixing duration (2- to 4-minute) is insignificant with respect to total organic and inorganic carbon removals.



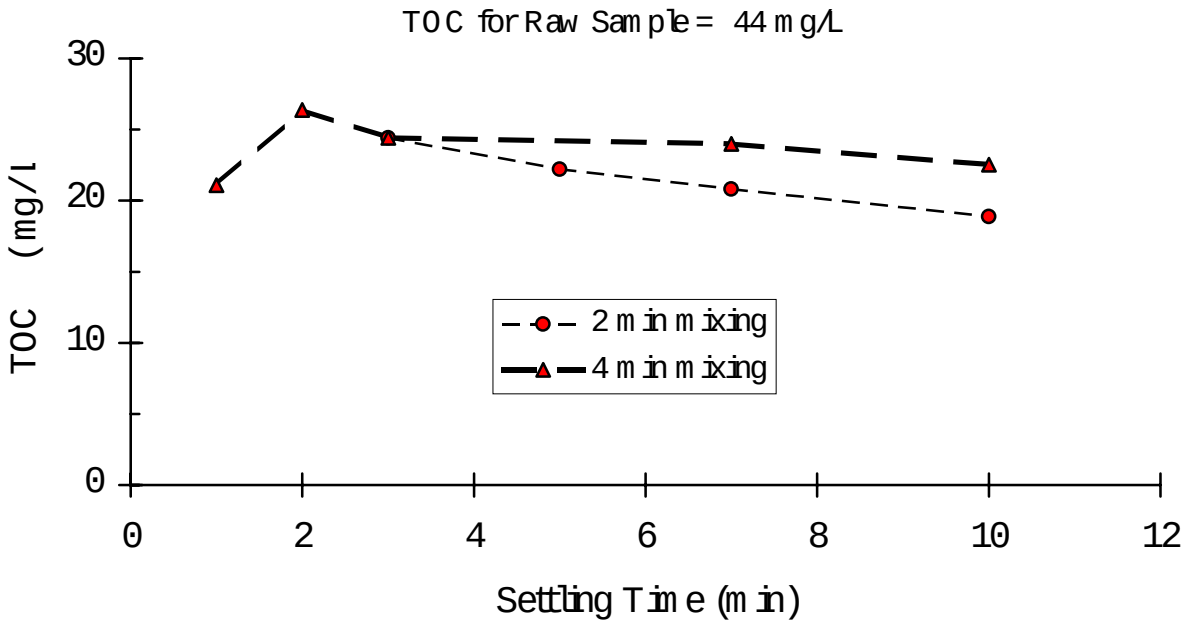
(A) Total Organic Carbon



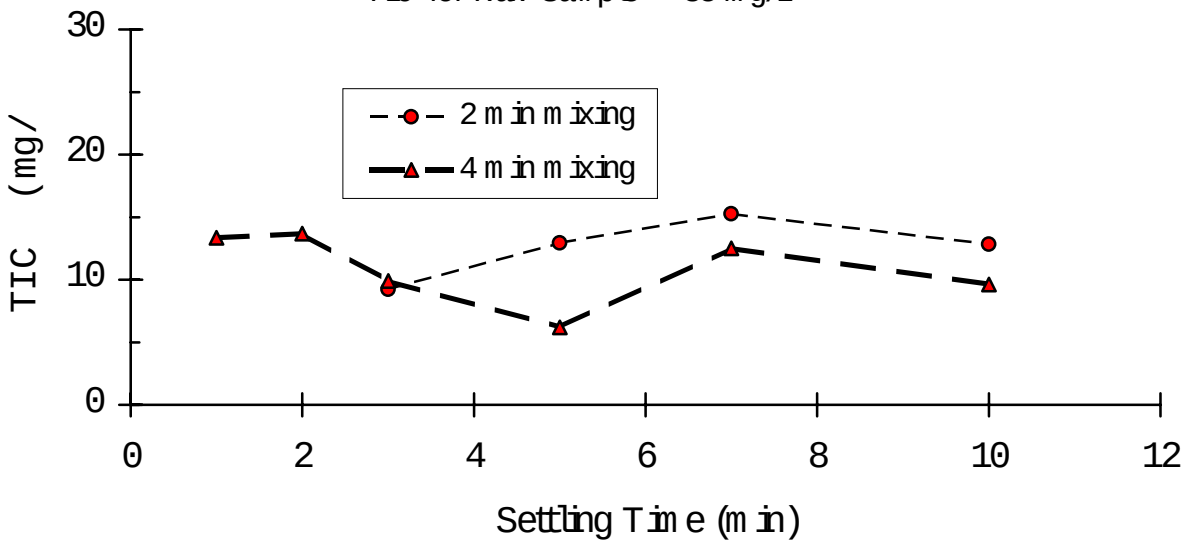
(B) Total Inorganic Carbon

MC-5: MC Size Range = 53—75 μm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 1 mg/L

Figure 5-17. Total Organic and Inorganic Carbon Distributions (with different raw samples)



(A) Total Organic Carbon



(B) Total Inorganic Carbon

MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L

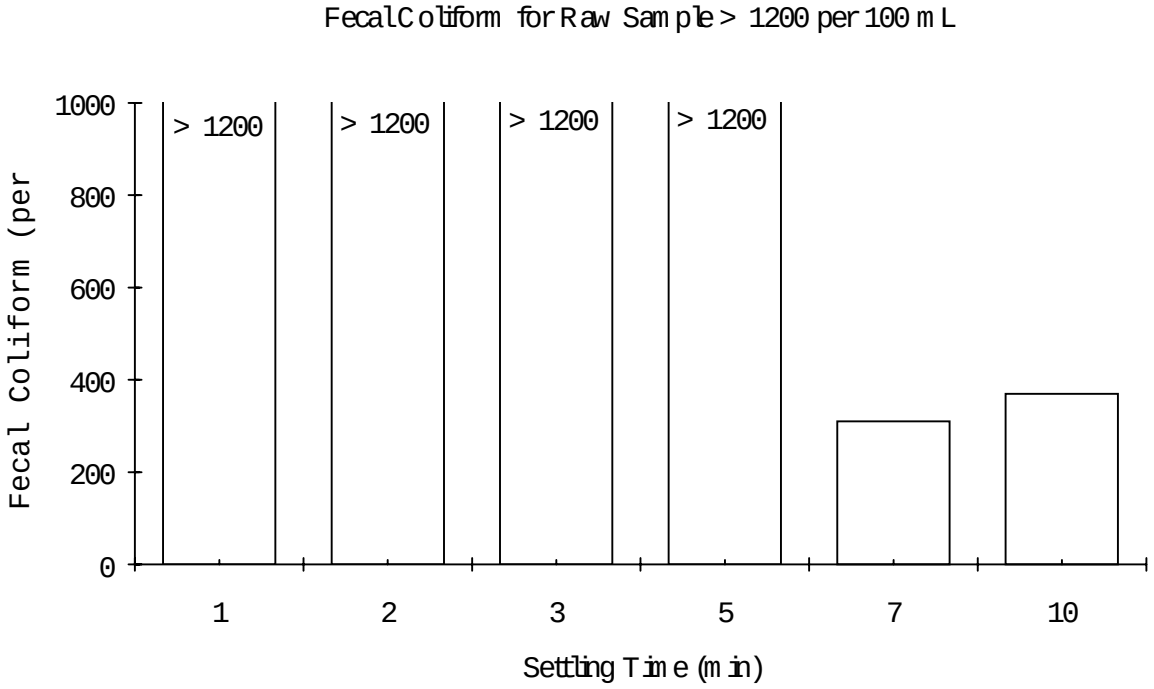
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}

PE-5: Polyelectolyte 309C Concentration = 6 mg/L

Figure 5-18. Total Organic and Inorganic Carbon Distributions (with different mixing duration)

Fecal Coliform

Figure 5-19 shows fecal coliform distribution versus settling time. It appears that for a 7-minute settling time, the fecal coliform is reduced to approximately 300 per 100 mL. The removal rate was observed as greater than 75% (considering the initial concentration was 1200 per 100 mL).



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration = 40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration = 6 mg/L

Figure 5-19. Fecal Coliform Distributions

Relationship of Particle Count Rate and Turbidity

Figure 5-20 illustrates the particle count rate distribution versus turbidity. A linear regression between these two parameters was performed and the correlation coefficient is 0.94, which indicates a strong relationship. Since the data ranges over more than two magnitudes, a log-log distribution of particle count rate and turbidity is shown in Figure 5-21. The log-log correlation of these two parameters was found to be 0.8. A log-log linear regression was also performed. The regression equations are expressed as follows:

$PCR = 3(Turbidity) + 4.4$ For linear regression
$Log(PCR) = 0.91 Log(Turbidity) + 0.54$ For log-log regression

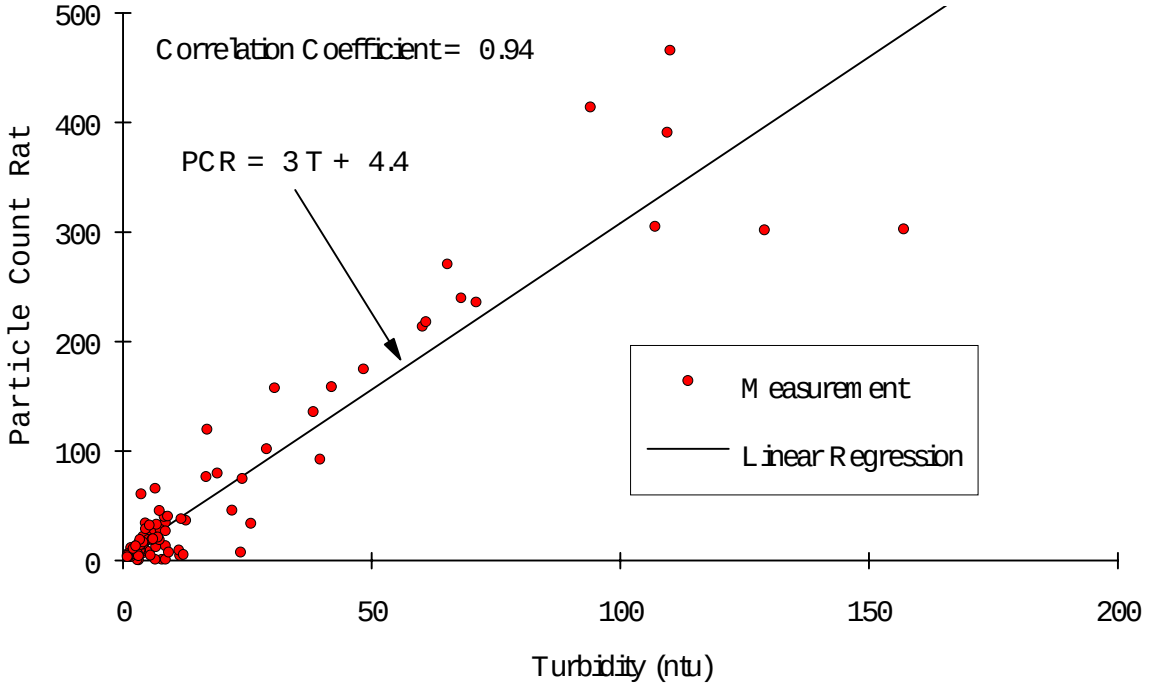


Figure 5-20. Particle Count Rate Versus Turbidity

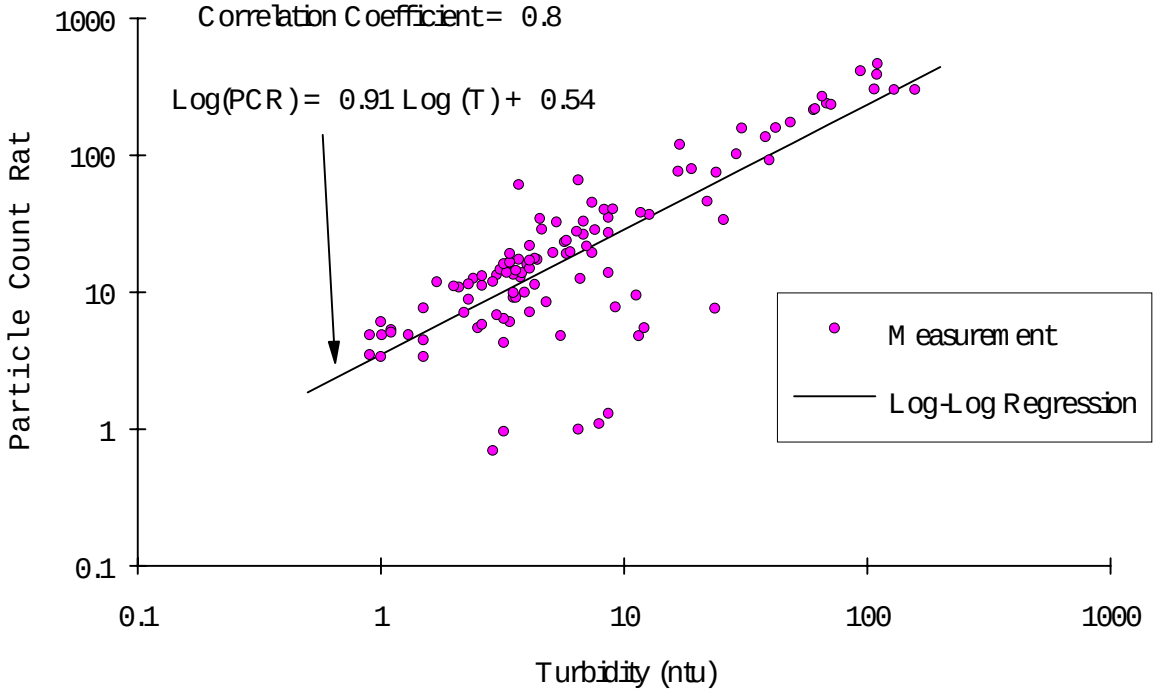
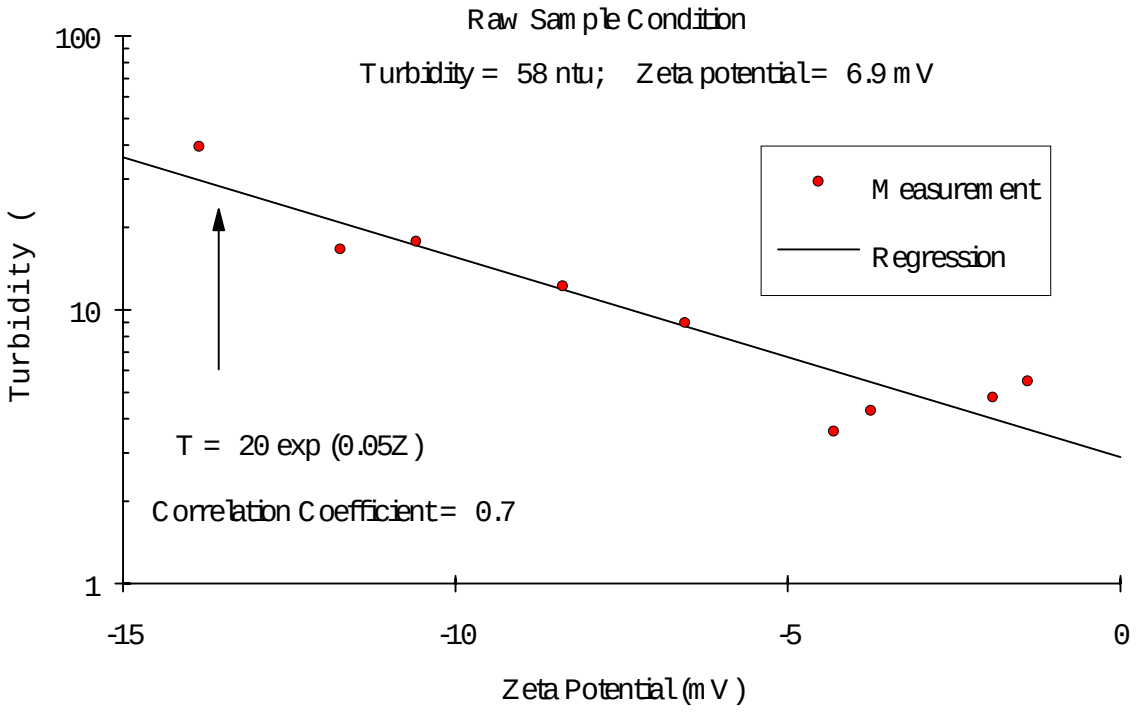


Figure 5-21. Particle Count Rate Versus Turbidity (log-log)

Zeta Potential

The relationship between zeta potential and turbidity is illustrated in Figure 5-22. It appears that the treatment is more effective when particles have less charge. A semi-log regression was performed based on test results. However, it was noted that in most CSO samples, zeta potential data fluctuated, which may be due to the varying charge characteristics of raw samples. The relationship between zeta potential and turbidity in CSO treatment is not as clear as in surface runoff treatment.



MC-5: MC Size Range = 53—75 µm; MC Concentration = 3 g/L
E-2: Ferric Chloride Concentration: 20—40 mg/L as Fe^{+++}
PE-5: Polyelectolyte 309C Concentration: 6—18 mg/L

Figure 5-22. Turbidity Distribution Versus Zeta Potential

Chapter 6
Summary and Recommendations

6.1 Summary

Based on the results of the MC weighted jar tests, the principal conclusions can be summarized as follows:

1. Conventional jar test procedure was modified to fit the MC weighted coagulation assessment.
2. In performing the MC weighted jar tests, three stages of mixing were used. First, a rate of 150 rpm with 10 seconds duration was used to mix coagulant with liquid and lift the MC from the bottom of the jar into suspension. Second, a mixing rate of 100 rpm with 10 seconds duration was used to mix flocculent and maintain the MC in suspension. Third, a rate of 60 rpm with 10 seconds duration was found to be sufficient for the flocculation process in treating storm runoff samples. In the CSO treatment process, one to two minutes was needed for the third stage (flocculation mixing).
3. For a better result of surface runoff treatment, the dosage of aluminum sulfate concentration was found to be 40 mg/L with the addition of 1 mg/L coagulant aid (flocculent).
4. From the CSO tests, the coagulant concentration was found to be 190 mg/L as $FeCl_3 \cdot 6H_2O$ or 40 mg/L as Fe^{+++} with the addition of 6 mg/L coagulant aid (flocculent).
5. Among the four MCs tested for surface runoff treatment, the MC in a size range of 53 to 150 μm at a dosage of 10 g/L yielded the best results in conjunction with the coagulant and polyelectrolyte. For the CSO treatment, MC in a size range of 53 to 75 μm at a dosage of 3 mg/L yielded better results.
6. After three minutes of settling, the following removal rates were achieved:

   (A) Surface runoff testing:
   - 98% for turbidity
   - 94% for particles smaller than 5 μm
   - 99% for particles larger than 2 μm
   - 83% for total solids
   - 95% for total volatile solids

   (B) CSO testing
   - 98% for turbidity
   - 98% for particles smaller than 5 μm
   - 99% for particles larger than 2 μm

- 99% for suspended solids
- 50% for total solids

7. Relationships between the zeta potential and turbidity were quantified by log-linear expressions for different conditions (as presented in Table 4-3).
8. The relationship between particle count rate and turbidity was quantified (as indicated in Figures 4-35, 5-20 and 5-21).
9. In view of high percentage of fine particles (< 5 μm) reduction in both storm runoff and CSO, one may conclude that the associated toxic heavy metals (as indicated in Table 1-1) might be substantially removed by the MC weighted coagulation.

6.2 Recommendations

The MC weighted coagulation is a new process, and many factors that affect the aspects of coagulation and flocculation bench-test (jar test) are still not well understood. For future studies, the following investigations are recommended:

1. Other types of coagulants and coagulant aids (flocculent or polyelectrolytes) should be evaluated.
2. In order to verify the effect of MC weighted coagulation on toxic heavy mattes removal as evidenced in the high percentage (> 90%) of fine particles (< 5 μm) reduction in MC jar test, measurement of additional parameters as listed in Table 1-1 should be included in experimental design as respond water quality parameters.
3. MC weighted coagulation kinetics should be studied in detail. The floc growth and shear rates are related to particle and floc concentrations and sizes, particle collision and stability coefficient, floc breakup constant, and velocity gradient. To investigate the flocculation kinetics, the velocity gradient, particle size and concentration should be controlled to evaluate the particle collision and stability coefficients as well as to develop a floc breakup constant. A model of MC kinetics should be investigated in order to develop greater MC process efficiency.
3. Prototype studies are necessary to expand the present bench scale level (i.e., jar testing) in order to provide engineering design parameters and operational procedures for utilization in a treatment plant. In order to perform on-site evaluation, a mobile unit should be developed for this purpose.

References

American Society for Testing and Materials. "Annual Book of ASTM Standards." Vol 11.01, Philadelphia, PA. 1996.

Association of Environmental Engineering Professors. "Environmental Engineering Unit Operations and Unit Processes laboratory Manual." University of Texas at Austin, Texas. 1971.

Black, A., A. Buswell, and F. Eidsness. "Review of the Jar Test." J. AWWA, Vol. 39, No. 11, pp 1414, 1957.

Black, A. and R. Harris. "New Dimensions for the Old Jar Test." *Water and Wastes Engineering*, Dec:49 (1969).

Boudries, H., C. Broguet, C., J-M. Mouchel, and D.R. Thévenot. "Urban Runoff Impact on Composition and Concentration of Hydrocarbons in River Seine Suspended Solids. " *Proc. 7thInt. Conf. on Urban Storm Drainage*. Hannover, Germany, 569-574. 1996.

Camp, T. "Floc Volume Concentration." *J. AWWA*, Vol. 60, No. 6, pp 656. 1968.

Chebbo, G., P. Musquere, V. Milisie and A. Bahoc (1990). "Characterization of Solids Transferred into Sewer Trunks During Wet Weather. " *Wat. Sci. Tech.*, 22(10/11) 231-240.

Clark, M. M. 1996. "Transport Modeling for Environmental Engineers and Scientists." John Wiley & Sons, Inc., NY.

Cohen, J. "Improved Jar Test Procedure." *J. AWWA*, Vol. 49, No. 11, pp 1425, 1957.

Derjaguin, B. and L. Landau. Theory of the Stability of Strongly Charged lyophobic Sols and of the Adhesion of Strongly charged Particles in Solutions of Electrolytes. *Acta Physicochim*. USSR, Vol. 14, pp 733-762, 1941.

Ellis, J.B. and Revitt, D.M. Incidence of Heavy Metals in Street Surface Sediments: Solubility and Grain Size Studies. *Water, Air, and Soil Pollution*, 17(1)87-95. (1982).

Estèbe, A., Belhomme, G., Lecomte, S., Videau, V., Mouchel, J-M., and Thévenot, D.R. "Urban Runoff Impacts on Particulate Metal Concentrations in River Seine: Suspended Solid and Sediment Transport." *Proc. 7th Int. Conf. on Urban Storm Drainage*, Hannover, Germany, 575-580. (1996).

Gregory, J. The role of Colloid Interactions in Solid-Liquid Separation. *Water Science and Technology*, Vol. 27, No. 10, pp 1-17,1993.

Han, M., and Lawler, D. F. Interactions of Two Settling Spheres: Settling Rates and Collision Efficiency. *Journal of Hydraulic Engineering*, Vol. 117, No. 10, pp 1269-1289, 1991.

Lopes, T. J. and Fossum, K. D. Selected Chemical Characteristics and Acute Toxicity of Urban Stormwater, Streamflow, and Bed Material, Maricopa County, Arizona. *Water-Resources Investigations Report 95-4074*, U.S. Geological Survey, Denver, Colorado (1995).

High Rate Microcarrier-Weighted Coagulation for Treating Wet Weather Flow

By

Chi-Yuan Fan [(1)], Yuan Ding[(2)], Shih-Long Liao [(3)], Richard Field [(4)], Paul C. Chan [(5)], and Robert Dresnack [(5)],

ABSTRACT

In wet-weather flow (WWF) a significant amount of toxic pollutants are associated with colloidal solids. Sedimentation with coagulation is considered to be an effective method of removing large quantities of suspended solids from water and wastewater. A new high-rate settling process, using microsand or a microcarrier (MC) as a settling carrier of colloids, has been developed and applied for treating both wet- and dry-weather flows (WWF/DWF). The addition and recirculation of the MC results in higher settling velocities and allowable tank overflow rates. The MC plays a crucial role in enhancing settling properties, and in particular, the removal of colloidal particles and associated contaminants.

A detailed testing procedure and a method of experimental analysis using a modified jar test for the MC process have been developed. A series of MC weighted jar tests were undertaken on parking lot storm runoff, synthetic samples, and combined sewer overflow (CSO) mixed with a MC, coagulant and coagulant aid. Two particle analyzers with a range of 0.002 to 5 micrometers (μm) and 0.1 to 2,000 μm, respectively, were used to determine the full range of particle size distribution. Different materials were used as the MC in this study. The operational parameters evaluated include coagulant dosage, coagulant aid type and dosage, mixing- and flocculation-induced hydraulic shear or velocity gradients and duration, and characteristics of the MC. The pH, turbidity, particle size distribution, total solids, total volatile solids, suspended solids, and zeta potential were determined. The experimental results revealed that MC weighted coagulation dramatically reduced coagulation-flocculation duration (< 3min) and settling time (< 8 min) producing flocs with high settling velocity and high quality supernatant. Reductions of turbidity from > 80 NTU (raw samples) to < 2 NTU (supernatant samples) were achieved.

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[(2)]Assistant Professor and [(5)]Professor, Department of Civil and Environmental Engineering, New Jersey Institute of Technology, Newark, NJ 07102.

INTRODUCTION

A significant amount of toxic pollutants in wet weather flow (WWF) are associated with smaller particles (< 10 μm), including toxic-organic chemicals (e.g., benzene, polynuclear aromatic hydrocarbons [PAH], and polychlorinated biphenyls [PCB]) and heavy metals (e.g., arsenic, cadmium, chromium, copper, lead, mercury, and zinc). Sedimentation with coagulation is generally considered to be an economical method of removing large quantities of suspended solids (SS) from water and wastewater. A new high-rate settling process, using microsand or a microcarrier (MC) as a settling carrier of colloids, has been developed and applied for treating both wet- and dry-weather flows (WWF/DWF). The addition and recirculation of MC will result higher settling velocities and allowable tank overflow rates. This process is also known as "ballasted-coagulation." It has been reported that an MC unit would increase solids removal by more than 80% at a range of overflow rates of 50 to 100 $m^3/h/m^2$ (20 to 40 gpm/ft^2). This high-rate process consists of the addition of MC, coagulant, and coagulant aid with the influent in a mixing chamber followed by coagulation-flocculation and sedimentation. The MC plays a crucial role in enhancing settling properties, and in particular, the removal of colloidal particles and associated contaminants.

Objectives. The objectives of this investigation were:

- Evaluate the applicability of conventional jar test procedure to the MC weighted coagulation, and if needed, modify the jar test procedure for screening MCs, coagulants, and coagulant aids;
- Test the effects of different types and dosages of coagulant and coagulant aid in conjunction with MC for selection of the most effective combination;
- Investigate the effect of MC on particle size distributions and zeta potential of colloids in urban WWF by using the modified jar test procedure.

METHODOLOGY

Materials

MC. Ottawa sand was selected, due to its abrasion resistance, and small and uniform size. The size range of Ottawa sand tested was between 100 and 500 μm. The MC size ranges and concentrations were determined by prescreening tests.

Coagulants. Alum (aluminum sulfate, $Al_2(SO_4)_3 \bullet 18H_2O$)and ferric chloride ($FeCl_3 \bullet 6H_2O$) were used as the coagulants for this study.

Coagulant Aids. Five polyelectrolytes from two different manufacturers were used in the experiments. Among them, four (POL-EZ-2466, POL-EZ-3466, POL-EZ-2696, and POL-EZ-7736, by Calgon Corporation, Pittsburgh, Pennsylvania) were used in surface runoff tests and one (309C, by Polydyne, Inc., Riceboro, Georgia) for combined sewer overflow (CSO) tests.

Apparatus and Instruments

The descriptions for the major test apparatus and analytical instruments used for the investigation, including the measured parameters, range, model number, and manufacturer, are briefly described as follows:

- Particle size analyzer I, designated as PSA-I (Master-Sizer X, Malvern Instruments Inc.), is a large particle size analyzer with a measurement range from 0.1 to 2000 μm.
- Particle size analyzer II, designated as PSA-II (90Plus with ZetaPlus, Brookhaven Instruments Corporation), is a small particle size analyzer with a measurement range from 0.002 to 5 μm. PSA-II is equipped with disposable sample cells that eliminates the cross sample residue influence.
- The zeta potential meter and PSA-II are integrated in one unit. The measurement range of the zeta potential meter is from 0.1 to 200 mV with the particle size range from 0.002 to 30 μm. The resolution is sample dependent and in the range of 0.1% to 5%.
- Jar test apparatus: A Phipps and Bird (Model PB-700^{TM}). Dimensions of each jar are 11.5 X 11.5 X 21 cm depth which is capable of testing a water sample volume of 2,000 ml. Each mixer is equipped with a flat stirring paddle (7.6 X 2.5 cm or 19.3 cm^2). The area of the paddle was increased to 38.7 cm^2 for the MC jar test in order to generate more rigorous turbulence for keeping the microsand in suspension.
- Turbidity meter.
- pH meter.
- Balance.

MC Weighted Jar Test

The procedures include the following steps:

1. Collect storm surface runoff sample, prepare synthetic sample, or CSO sample. Measure the sample for pH and turbidity.
2. Pour 1,000 ml of the water sample into each two-liter jar of the jar-test apparatus and check stirrer operation. A light table facilitated viewing the contents of the jars.
3. Add controlled amounts (dosages) of MC, coagulant, and coagulant aid to the jars.
4. Flash mix for 20 to 60 s at 100 to 200 rpm.
5. Slow mix for 10 to 120 s at 30 to 60 rpm. Record the elapsed time before a visible floc is formed. If large flocs are formed, reduce the paddle speed. Record the appearance of the floc formed.
6. After flocculation, remove paddles and settle for 2 to 30 min.

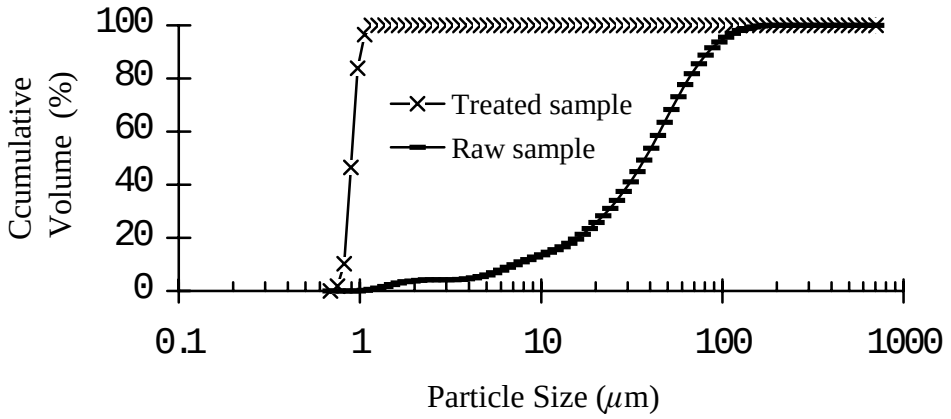
7. Collect the supernatant from the sampling port on each jar and measure turbidity; the settled solids should not be disturbed during sampling. Select and record the dosage of coagulant and coagulant aid based on the supernatant clarity and settleability of floc.

RESULTS

The followings summarize the results of MC jar tests with surface runoff and CSO:

Surface Runoff

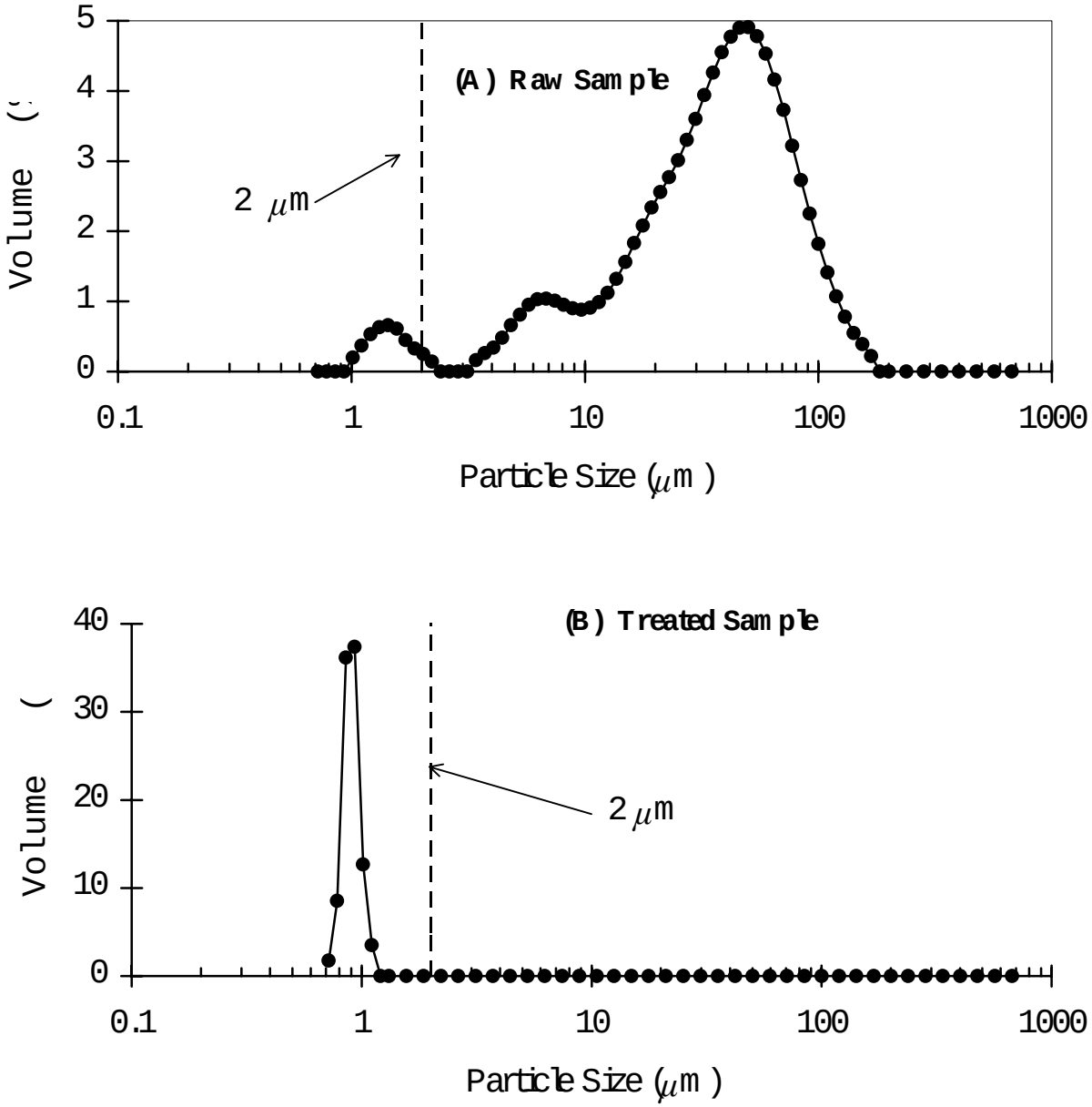
Figure 1 illustrates cumulative volume distributions versus particle size before and after the MC weighted coagulation. For the raw sample (before treatment), the measurable range of particle size is from 1 to 170 μm which consists of 81% from 10 to 100 μm and 14% smaller than 10 μm. After the MC coagulation, the particles in the supernatant of the jar were found to be < 2 μm, which indicated that all particles > 2 μm were removed.



MC Size Range: 53 to 150 μm; MC Concentration: 3 g/L
Aluminum Sulfate Concentration: 40 mg/L
Cationic Polyelectrolyte (POL-EZ-2466) Concentration: 1 mg/L

Figure 1. Particle Sizes of Raw and Treated Surface Runoff Samples (Cumulative)

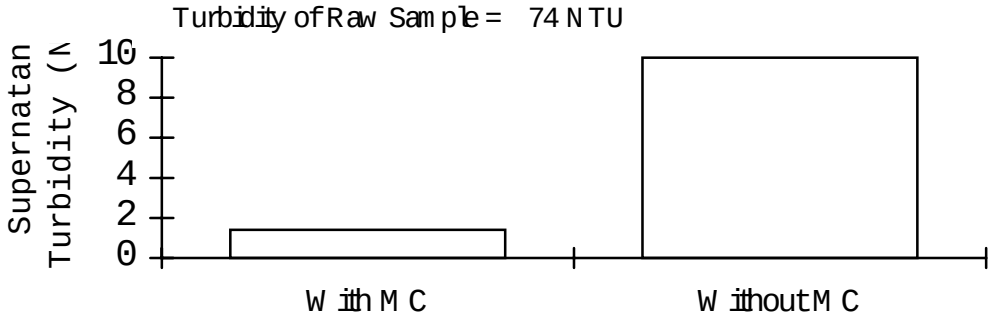
Figure 2 (A) and (B) illustrate the particle size distribution characteristics of the raw sample and supernatant sample after MC treatment, respectively. For the raw sample, the distribution peak is at approximate 50 μm while the small particles (from 0.7 to 2 μm) were either undetectable or only at a low percentage compared to the peak. After treatment, only particles < 2 μm remained in the supernatant. Since the larger particles were all removed from the raw sample, the percentage of particles < 2 μm increased significantly. The removal efficiency for particles < 2 μm was measured by the particle count rate (PCR) that is directly related to the number of particles counted per unit time in a solution expressed as kilo-count per second (kcps). Results of PCR are indicated in Figure 3.



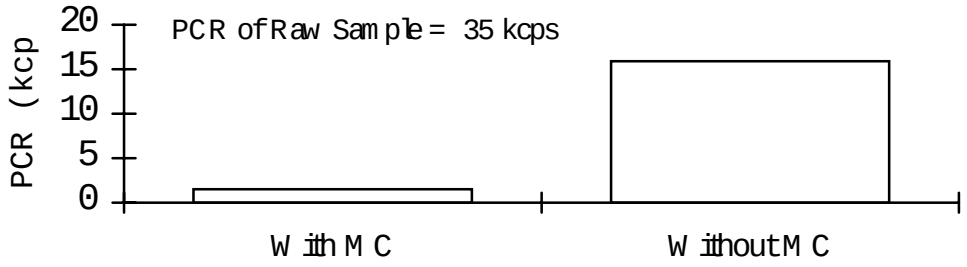
MC Size Range: 53 to 150 μm; MC Concentration: 3 g/L
Aluminum Sulfate Concentration: 40 mg/L
Cationic Polyelectrolyte (POL-EZ-2466) Concentration: 1 mg/L

Figure 2. Particle Size of Raw and Treated Surface Runoff Samples (Distributions)

MC jar tests were conducted with both coagulants and coagulant aids. Figure 3 (A) and (B) present supernatant turbidity and PCR results with and without MC. Both turbidity and PCR of supernatant samples with MC are much lower than those without MC. It is apparent that the addition of MC improves the treatment process effectively.



(A) Coagulant Aid (Anionic Polyelectrolyte [POL-EZ-7736])



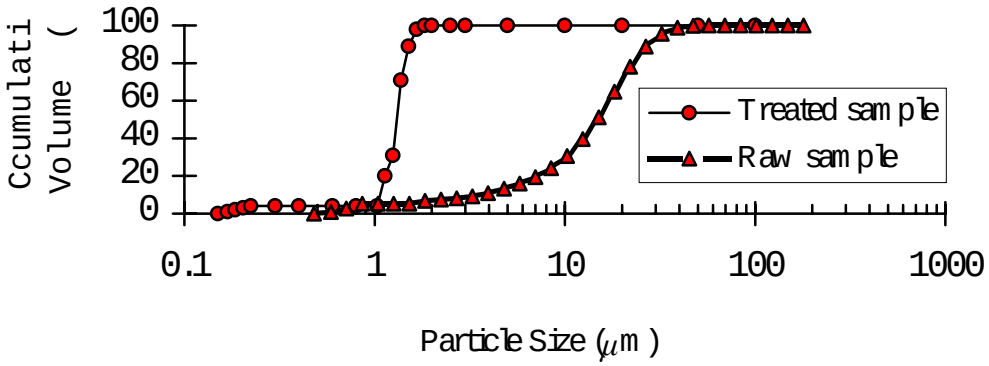
(B) Coagulant Aid (Non-ionic Polyelectrolyte [POL-EZ-2696])

MC Size Range: 53 to 150 µm; MC Concentration: 3 g/L
Aluminum Sulfate Concentration: 40 mg/L
(A) and (B) Coagulant Aid Concentration = 1 mg/L

Figure 3. Effectiveness of the MC Process (Surface Runoff Samples)

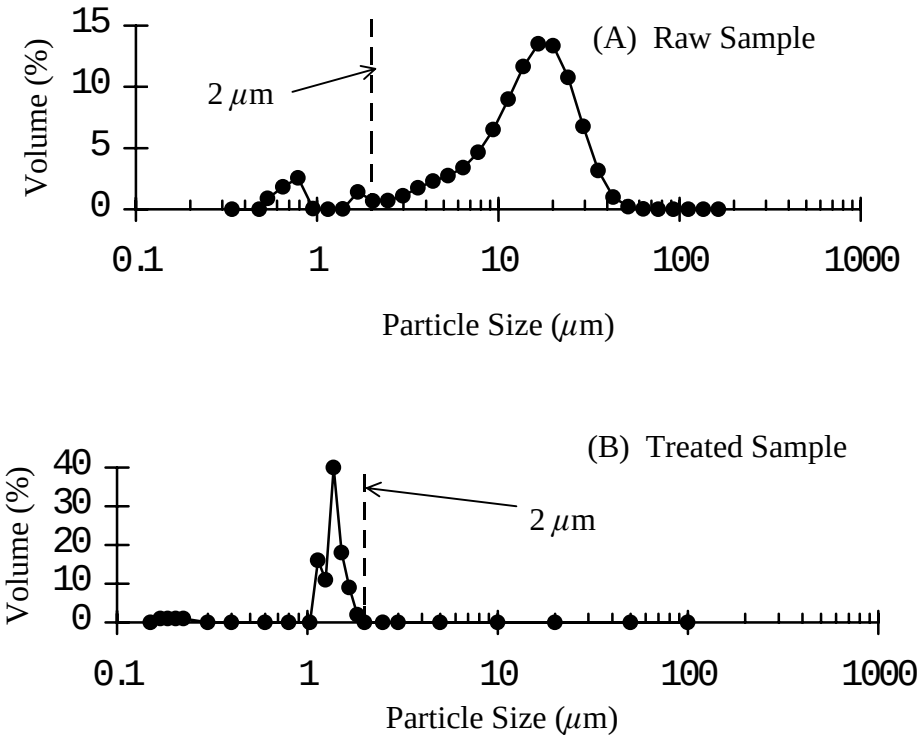
CSO

Figures 4 and 5 illustrate cumulative and discrete volume distributions versus particle size of raw sample and supernatant after MC weighted coagulation, respectively. For the raw sample (before treatment), the measurable range of particle size is from 0.5 to 60 µm with 93% (by volume) > 2 µm. After the MC coagulation, the particles in the supernatant of the jar were found to be < 2 µm, indicating all particles > 2 µm were removed.



MC Size Range: 53 to 75 μm; MC Concentration: 3 g/L
Ferric Chloride Concentration: 40 mg/L(as Fe^{+++})
Cationic Polyelectrolyte (309C) Concentration: 1.5 mg/L

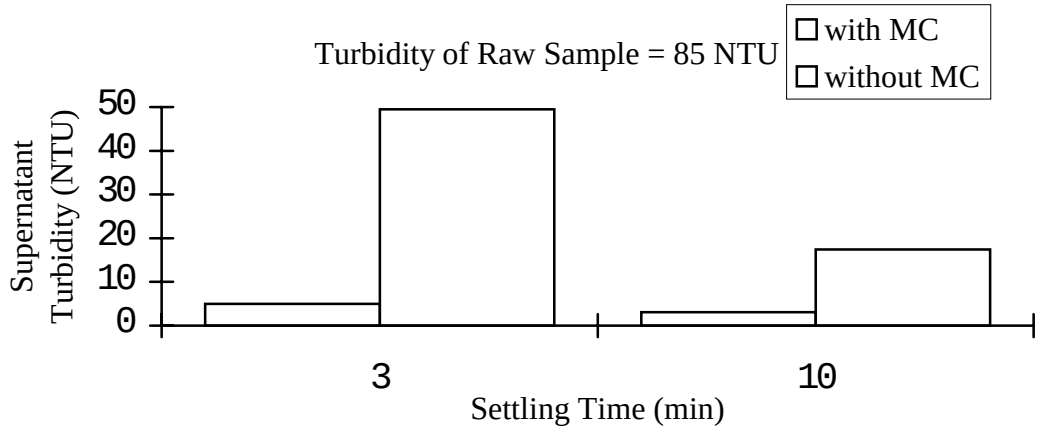
Figure 4. Particle Sizes of Raw and Treated CSO Samples (Cumulative)



MC Size Range: 53 to 75 μm; MC Concentration: 3g/L
Ferric Chloride Concentration: 40 mg/L (as Fe^{+++})
Cationic Polyelectrolyte (309C) Concentration: 1.5 mg/L

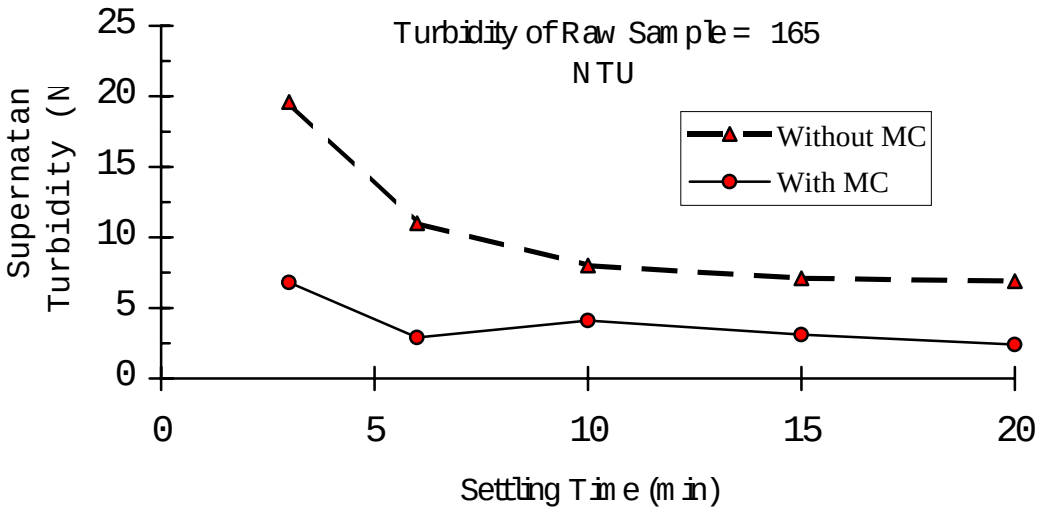
Figure 5. Particle Sizes of Raw and Treated CSO Samples (Distributions)

The effect of the MC was evaluated using turbidity and particle size distribution as indicating parameters. Figure 6 presents results of supernatant turbidity versus settling time with and without MC.



MC Size Range: 53 to 75 µm; MC Concentration: 3 g/L
Ferric Chloride Concentration: 40 mg/L (as Fe^{+++})
Cationic Polyelectrolyte (309C) Concentration: 1 mg/L

Figure 6. Effect of MC on CSO Samples



MC Size Range: 53 to 75 µm; MC Concentration: 3 g/L
Ferric Chloride Concentration: 40 mg/L (as Fe^{+++})
Cationic Polyelectrolyte (309C) Concentration: 1 mg/L

Figure 7. Turbidity versus Setting Time

CONCLUSIONS

Based on the results described above, conclusions can be summarized:

1. A testing procedure for experimental analysis of the MC process has been developed.
2. The MC process was found to be effective in reducing coagulation-sedimentation time, which, in turn, will reduce the sizing requirements of the process needed compared to a conventional physical-chemical treatment facility. The total treatment time could reduce to $<$ 10 min utilizing the MC-weighted coagulation-sedimentation process. Although stormwater and CSO samples with varying influent characteristics can be anticipated to react differently to the MC process, it is expected that the tremendous reduction in settling time found in this study will generally extend (in varying degrees) to all storm runoff and CSO samples.
3. In performing the MC-weighted jar tests (i.e., the modified jar test developed under this study), three stages of mixing, with 10 s duration in each stage, were used: (1) 150 rpm to lift the MC from the bottom of the jar into suspension, (2) 100 rpm to keep the MC in suspension, and (3) 60 rpm for the coagulation-flocculation process to treat storm runoff samples. For CSO treatment, the third stage duration for coagulation-flocculation was found to be optimal at 1 to 2 min.
4. The best combination coagulant/coagulant aid in the surface runoff MC study, was found to be 40 mg/L aluminum sulfate (coagulant) and 1 mg/L cationic polyelectrolyte, POL-EZ-2466 (coagulant aid). For CSO 40 mg/L coagulant (ferric chloride, as Fe^{+++}) with 1 mg/L coagulant aid (cationic polyelectrolyte, 309C) resulted in the best turbidity removal.
5. In the MC size and concentration study, the range of 53 to 150 μm at a dosage of 10 g/L yielded the best results for surface runoff. For CSO treatment, MC in a size range of 53 to 75 μm at a dosage of 3 g/L resulted in the lowest supernatant turbidity.

RECOMMENDATIONS

The following is recommended for the future:

1. Additional jar tests to refine the MC coagulation process for removal of toxic pollutants and microorganisms in urban WWF with different types of coagulant and coagulant aid.
2. Pilot studies to verify and expand upon the present bench-scale level (i.e., jar testing) in order to provide engineering design and operational procedures for full-scale MC systems.

BIBLIOGRAPHIES

1. American Society for Testing and Materials. 1996. *Annual book of ASTM standards*, Vol. 11.01, Philadelphia, PA.

2. Association of Environmental Engineering Professors. 1984. *Environmental engineering unit operations and unit processes laboratory manual*, University of Texas at Austin, Texas.

3. ASCE and AWWA, 1971. *Water treatment plant design*, AWWA Inc., Denver, CO

4. Black, A., Buswell, A., and Eidsness, F. 1957. "Review of the Jar Test," *J. AWWA*, Vol. 39, No. 11, p. 1414.

5. Black, A. and Harris, R. 1969. "New dimensions for the old jar test," *Water and Wastes Engineering*, Dec:49.

6. Camp, T. 1968. "Floc volume concentration," *J. AWWA*, Vol. 60, No. 6, p. 656.

7. Cohen, J. 1957. "Improved jar test procedure." *J. AWWA*, Vol. 49, No. 11, p. 1425.

8. Guibelin, E. 1994. "Actiflo process: a highly compact and efficient process to prevent water pollution by stormwater flows," *Water Science and Technology*, Vol. 30, No. 1 .

9. "*Methods for chemical analysis of water and wastes*," EPA-600/4-79-020, Revised March 1983.

10. *Standard Methods for the Examination of Water and Wastewater*, 18th edition supplement, 1995. American Public Health Association, Washington, DC.

Maltby, L., *et al.* The Effects of Motorway Runoff on Freshwater Ecosystems: 1. Field Study. *Environ. Toxicol. And Chem.* 14(6):1079 (1995).

McGregor, I., Ashley, R. M., and Oduyemi, K. O. K., Pollutant Release from Sediments in Sewer Systems and Their Potential for Release into Receiving Waters. *Wat. Sci. Tech.* 28(8/9)161-168 (1993).

O'Melia, C. R. and Tiller, C. L. "Physicochemical Aggregation and Deposition in Aquatic Environmental." in *Environmental Particles*, Vol. 2, Edited by Buffle, J. and van Leeuwen, H., Lewis Publishers, N.Y. 1993.

Pitt, R., R. Field, M. Lalor, and M. Brown Urban Stormwater Toxic Pollutant Assessment, Sources, and Treatability. *Water Environ. Research*. 67(3) 260-275 (1995).

Pruppacher, H. R., and J.D. Klett. *Microphysics of Clouds and Precipitation*. D. Reidel Publishing Company, Dordrecht, Holland, 1978.

Russel, W. B., D. A. S. Saville, and W.R. Schowalter. *Colloidal Dispersions*. Cambridge University Press. NY. 1989.

Sansalone, J.J., *et al.* Correlations Between Heavy Metals and Suspended Solids in Highway Runoff: Implications for Control Strategies. *Transportion Research Record*, 1483(7):12, 1995.

Standard Methods for the Examination of Water and Wastewater, 18th edition supplement. American Public Health Association, Washington, DC. 1995.

Stumm, W. and J. Morgan. *Aquatic Chemistry*. Third edition. Wiley, N.Y. 1995.

U.S. Environmental Protection Agency *Methods for Chemical Analysis of Water and Wastes,* EPA-600/4-79-020. Cincinnati, OH 1983.

Verwey, E. J. W. and J. Overbeek. *Theory of the Stability of Lyophobic Colloids*, Elsvier Publisher, N.Y. 1948

Vignoles, M. And L. Herremans. Metal Pollution of Sediments Contained in Runoff Water in the Toulouse City. *NOVATECH 95, Second International Conference on Innovative Technologies in Urban Storm Drainage,* May 30-June 1, 1995. Lyon, France, Organized by Eurydice 92 and GRAIE. 611-618.

Wen, C. S. *The Fundamentals of Aerosol Dynamics.* World Scientific Publishing Co, River Edge, NJ, 1996.